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**Investigation of Selected Potential
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Butadiene and Its Oligomers**

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Investigation of Selected Potential Environmental Contaminants: Butadiene and Its Oligomers

By:

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December 1978

Final Report

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Prepared For:

**Office of Toxic Substances
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16. ABSTRACT This report is a survey and summary of the literature on butadiene and its oligomers. Major aspects of their biological effects, environmental exposure, chemistry, production and use, and regulations are reviewed and assessed. Butadiene is a reactive gas used primarily in the production of rubbers and resins; over 3 billion pounds are produced annually in the U.S. Among other reactions, it undergoes self-condensation to form cyclic oligomers, such as 4-vinylcyclohexene, 1,5,9-cyclododecatriene, and 1,5-cyclo-octadiene. The latter is used primarily as a precursor to nylon; the other oligomers are less important commercially. Vinylcyclohexene, however, is a contaminant in butadiene. Limited monitoring data indicate that low levels of butadiene enter the environment during production, end-use, storage and transport; it has been identified as a minor constituent of urban air and gasoline. The high degree of chemical reactivity of butadiene precludes environmental persistence. In humans, exposure to butadiene vapor may result in lethargy and drowsiness, as well as irritation to the eyes and mucous membranes. There have been no reports in the U.S. or Western Europe of long-term effects of butadiene arising from occupational exposure. Poorly documented cases of gastrointestinal tract, and circulatory and nervous system disorders have been reported in Russian synthetic rubber workers; butadiene has been implicated as a causative factor. Butadiene intoxication may cause narcosis in laboratory mammals; few adverse effects have been reported for chronic exposures. Few toxicity data are available for the oligomers.		
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PREFACE

This report is a survey and a summary of the literature on butadiene and its oligomers available through June, 1978. Major aspects of chemistry, commercial production, environmental exposure, biological effects and regulations are reviewed. Appendix A lists sources of information employed.

This document was prepared by the Franklin Research Center for the U.S. Environmental Protection Agency under contract number 68-01-3893.

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EXECUTIVE SUMMARY

Butadiene (BD) is a reactive gas used primarily in the production of rubbers and resins. Over 3 billion pounds are produced annually in the U.S. Among other reactions it undergoes self-condensation to form cyclic oligomers, such as 4-vinylcyclohexene, 1,5,9-cyclododecatriene and 1,5-cyclooctadiene. The latter is used primarily as a precursor to nylon; the other oligomers are less important commercially. Vinylcyclohexene, however, is a contaminant in butadiene.

Limited monitoring data indicate that low levels of butadiene enter the environment during production, end-product use, storage and transport. It has been identified as a minor constituent of urban air and gasoline. The high degree of chemical reactivity of butadiene, including reactions with light, ozone, and nitrogen oxides, precludes environmental persistence.

In humans, exposure to butadiene vapor may result in lethargy and drowsiness, as well as irritation to the eyes and mucous membranes. Skin contact may cause frostbite due to rapid evaporation. There have been no reports in the U.S. or Western Europe of long-term effects of butadiene arising from occupational exposure. Poorly documented cases of gastrointestinal tract, and circulatory and nervous system disorders have been reported in Russian synthetic rubber workers; butadiene has been implicated as a causative factor.

Based primarily on low toxicity to laboratory animals, occupational exposure in the U.S. is limited to 1,000 ppm BD ($2,200 \text{ mg/m}^3$) (8-hour time-weighted average). In laboratory mammals, butadiene intoxication may cause narcosis. In long-term studies, few adverse effects were reported by American investigators who exposed animals to high levels of butadiene (up to $14,807 \text{ mg/m}^3$) for as long as 8 months. Several Russian investigators,

however, reported adverse effects in rats exposed to only 30 mg/m^3 for less than 3 months. Some of these changes included decreased weight gain, decreased activity, enzyme and blood alterations, and organ changes (especially in the lung, spleen, kidney and heart). No tests for carcinogenicity are available for butadiene.

In a recent study, butadiene showed mutagenic activity in two of 6 bacterial strains tested. Butadiene has a low toxicity to plants. Its effects on marine animals are unknown.

Few toxicity data are available for butadiene oligomers. Toxic effects on the skin have been noted for vinylcyclohexene, cyclooctadiene and cyclododecatriene in mammals.

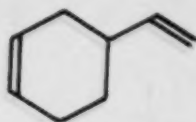
I. PHYSICAL AND CHEMICAL DATA

A. Chemical Structure

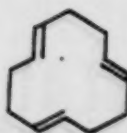
1,3-Butadiene is a conjugated diene of the following structure:
 $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. Cis and trans conformations are in equilibrium at room temperature, but trans predominates (Aston and Szasz, 1946). Bond distances were reported by Almennigen et al. (1958), among others, as: C-H, 0.1082 nm C-C, 0.1483 nm; and C=C, 0.1337 nm.

Butadiene reacts with itself in the presence of free-radical inhibitors yielding low molecular weight cyclic oligomers. Examples of butadiene oligomers are given below:

4-Vinylcyclohexene (VCH)



1,5,9-Cyclododecatriene (CDT)



1,5-Cyclooctadiene (COD)



1,2-Divinylcyclobutane



Synonyms and other identifiers of butadiene and its oligomers are given in Table 1.

Table 1
Nomenclature and Other Identifiers of Butadiene and Oligomers

Chemical Abstracts Service 9th Collective Index name:	1,3-Butadiene	Cyclohexene, 4-Ethenyl-a	Cyclobutane, 1-2-diethenyl	1,5,9-Cyclododeca- triene ^a	1,5-Cyclo- octadiene
CAS Registry No.:	106-99-0	100-40-3	2422-85-7; cis: 16177-46-1; trans: 6553-48-6	4904-61-4; Z,Z,Z; 4736-48-5; E,Z,Z; 2765-29-9; E,E,Z; 706-31-0; E,E,E; 676-22-2	111-78-4; Z,Z; 1552-12-1 E,Z; 5259-71-2
EPA Toxic Substances Substance Control Act List No:	R037-0754	R030-8445	-	R161-8363	R041-6655
Synonyms:	Alpha,Gamma- Butadiene Biethylene Divinyl Buta-1,3-Diene Butadiene Divinyl Erythrene Pyrrolylene Vinylethylene	Butadiene Dimer 1-Ethenyl- cyclohexene 1,2,3,6-Tetra- hydrostyrene 4-Vinyl-1- cyclohexene 1-Vinylcyclo- hexene 1-Vinyl-3- cyclohexene 1-Vinyl-Cyclo- hexene-3 VCH	Divinylcy- clobutane	CDT	COD
Molecular Formula:	C ₄ H ₆	C ₈ H ₁₂	C ₈ H ₁₂	C ₁₂ H ₁₈	C ₈ H ₁₂
Viscuser Line Notation:	IU 2 UI	L6UTJ DIUI	L4TJ AIUI BIUI L4TJ AIUI CIUI LUTJ AIUI XIUI	L-12-U EU IUTJ	L8U EUTJ

^a referred to in text as 4-vinylcyclohexene or vinylcyclohexene
^b referred in 8th collective index as t,t,t for Z,Z,Z; c,t,t for E,Z,Z; c,c,t for E,E,Z; c,c,c for E,E,E

B. Properties of the Pure Material

Butadiene is a colorless gas at room temperature with a mild aromatic odor. It is only slightly soluble in water (Figure 1), more soluble in methanol and ethanol but readily soluble in acetone, ether, benzene, carbon tetrachloride, chloroform, furfural etc. (Kirshenbaum and Kahn, 1964). It is extremely flammable, forming explosive mixtures with air at about 2.0 to 11.5 percent by volume (explosive range). Ignition can occur readily as the flash point is below 0°C . Physical properties of butadiene and its oligomers are summarized in Tables 2 and 3.

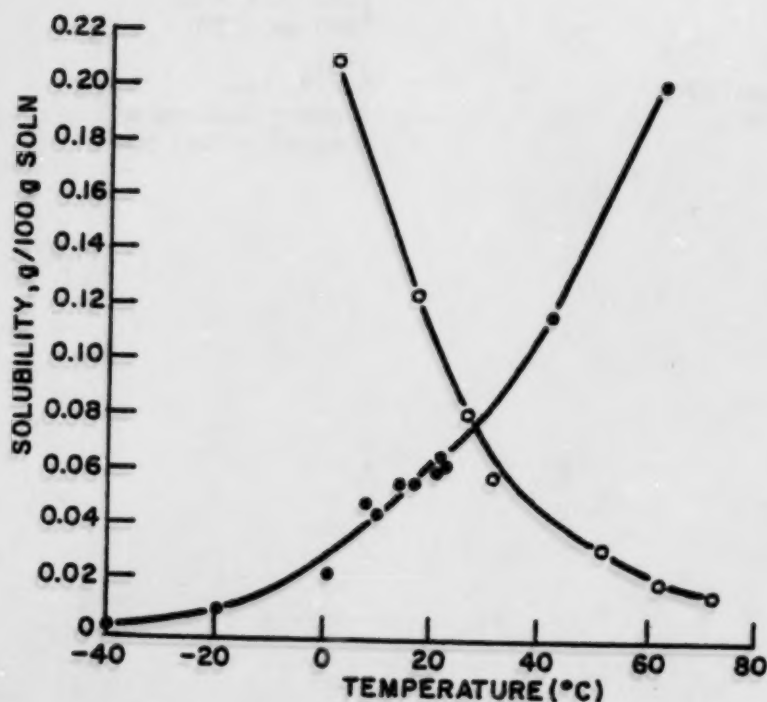


Figure 1. Solubility of Butadiene. Closed Circle: solubility of water in liquid Butadiene; Open Circle: solubility of gaseous butadiene at 760 mm Hg in water. (adapted from Bailey, 1971)

Table 2
Physical Properties of Butadiene
(Kirshenbaum and Kahn, 1964)

Appearance	Colorless gas or liquid, mild aromatic odor
Boiling Point, 760 mm Hg	- 4.413°C
Critical Temp.	152°C
Critical Press.	42.7 atm.
Density	
20°C	0.6211 g/ml
25°C	0.6149 g/ml
Flash Point	<-18°C
Flammable Limits	2-11.5% by volume in air
Freezing Point, 760 mm Hg	-108.915°C
Heat of Formation, 25°C	
gas	26.33 kcal/mole
liquid	21.21 kcal/mole
Melting Point	-108.91
Molecular Weight	54.09
Solubility in Water	0.037 wt% at 10°C
Vapor Density	1.88 (air = 1)
Vapor Pressure	1900 mm, 20°C
% Volatile	100%
Weight/U.S. gallon, 16°C	5.229 lbs.
Conversion Factors	1 ppm = 2.21 mg/m ³ 1 mg/m ³ = 0.45 ppm

Table 3

Physical Properties of Butadiene Oligomers
(Wilke, 1963; Weast, 1975; Bengeladorf et al., 1960,
McAuliffe, 1966; Coffey, 1968)

	Vinylcyclohexene		1,5,9-Cyclododecatriene		1,5-Cyclooctadiene ^a
	Z,Z,Z	E,E,E	Z,Z,Z	E,E,E	
Boiling Point (°C)	50-52 ^b 145 ^c	96 ^d	98 ^d	106 ^d	91.5 ^e
Flash Point	21°C, open cup	80°C for mixture of isomers			37.8
Freezing Point	-109°C	-	-	-	-
Melting Point	-101°C	+34°C	-16.8°C	-9 to -8°C	-70
Molecular Weight	108.18	162.27	162.27	162.27	108.18
Refractive Index, n_D^{20}	1.4915	1.5005	1.5078	1.5129	(a)
Solubility	immiscible with water, miscible with ether, ben- zene and methanol; solubility in	soluble in hydrocarbons			soluble in hydrocarbons
	water: 50 ± 5 g/10 ⁶ g H ₂ O				
Vapor Pressure Weight/U.S. Gallon, 16°C	20 mm at 31°C	7.35 lb.	7.35 lb.	7.35 lb.	5 mm Hg at 20°C 7.35 lb.

^a Properties for isomers not specified except for refractive index
(t, t = 1.4975; c, c = 1.4910)

b at 22 mm Hg

c at 760 mm Hg

d at 10 mm Hg

e at 127 mm Hg

C. Properties of the Commercial Material

Commercial grade butadiene is >98% pure. Specifications for butadiene available from one manufacturer are given in Table 4. Vinylcyclohexene is present as an impurity at a maximum of 0.2%. Other impurities include vinyl acetylenes, aldehydes, C₅ hydrocarbons, peroxides, sulfides and nonvolatile matter. DiCorcia et al. (1977) identified 20 impurities in pure-grade butadiene (Table 5). An inhibitor of peroxide formation (usually 100 ppm p-tertiary butyl catechol) is added when butadiene is offered for shipment.

Table 4
Specifications and Typical Inspections
for 1,3-Butadiene Inhibited with
p-Tertiary Butyl Catechol (Exxon, 1973)

	<u>Specification</u>	<u>Typical Inspections</u>
Acetylenes, alpha, as vinyl acetylenes (ppm)	500 Max	150 Max
Acetylenes, vinyl (ppm)	10 Max	0-5
Appearance	Clear and Free of Suspended Matter	-
Butadiene Dimer (weight percent)	0.2 Max	0.01
Carbonyl, as acetaldehyde (ppm)	50 Max	<20
Conjugated Diene, as 1,3 butadiene (wt %)	99.0 Min	99.1
Hydrocarbons - C ₅ (weight percent)	0.05 Max	0.01
Nonvolatile Matter (weight percent)	0.1 Max	0.01
Peroxides, as hydrogen peroxide (ppm)	10 Max	Nil
Sulfur, as hydrogen sulfide (ppm)	10 Max	Nil

Vinylcyclohexene is available as technical grade (95% purity) or research grade (99% purity). The most likely contaminants are cyclooctadiene and the hydroperoxide of vinylcyclohexene (1-hydroperoxy-4-vinylcyclohexene) (IARC, 1976). Non-volatiles are present at 0.03% by weight. An oxidation inhibitor (50 ppm t-butylcatechol) is added.

1,5,9-Cyclododecatriene and 1,5-cyclooctadiene are available commercially at a purity of 98% by weight. Both products are inhibited with

Table 5
Impurities in Pure-Grade 1,3-Butadiene
(DiCorcia et al., 1977, DiCorcia and Samperi, 1975)^a

<u>Impurities</u> ^b	<u>Levels (ppm)</u>
methane	10
ethane	7
ethylene	12
acetylene	0.3
cyclopropane	0.4
propane	5
propene	46
propadiene	70
propyne	13
isobutane	n.r.
neo-pentane	n.r.
butane	210
1-butene	5500
isobutene	2500
1,2-butadiene	n.r.
2-cis-butene	270
2-trans-butene	390
1-butine	n.r.
1-butene-3-ine	n.r.

^a List of impurities taken from both references; levels are reported in DiCorcia and Samperi (1975) only, so levels for all impurities in Table 5 are not known, and identified as n.r. (not reported).

^b Identification was carried out using a gas chromatograph equipped with a flame ionization detector.

t-butylcatechol (at 60 ppm and 50 ppm, respectively). Commercial cyclooctatriene consists of the trans, trans, trans (56%) and the cis, trans, trans isomers (36%). Vinylcyclohexene is an impurity in commercial cyclooctadiene (Reichel et al., 1963), and nonvolatiles total 0.03% by weight (Citco, 1969).

D. Reactions Involved in Use

1. Butadiene

Butadiene is probably one of the most thoroughly investigated chemicals; several thousand reactions of butadiene have been recorded in the literature (Baily, 1971). Commercial use primarily involves polymerization, but other industrial reactions are also summarized in the sections which follow.

a. Polymerization

Butadiene polymers include polybutadiene, styrene-butadiene rubber and latices (SBR), acrylonitrile-butadiene or nitrile rubber, and acrylonitrile-butadiene-styrene (ABS) resins. Structures of these butadiene polymers are shown in Table 6. Manufacture and use are discussed in Section II-A.

b. Dimerization to Vinylcyclohexene and Cyclooctadiene

Butadiene undergoes a wide variety of Diels-Alder reactions, the addition of an activated olefin (dienophile) to the 1,4 positions of a diene forming a six numbered ring. An example is dimerization, in which butadiene acts as both a diene and a dienophile to form 4-vinylcyclohexene. Catalysts are not required for dimerization nor is the reaction inhibited by t-butylcatechol, the peroxide inhibitor added to commercial butadiene (Saltman, 1965). Vinylcyclohexene is always found as an impurity in butadiene and is a common

Table 6

Structure of Several Butadiene-Containing Polymers

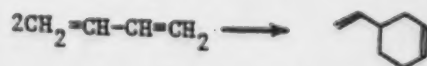
<u>Name</u>	<u>Structure</u>
Polybutadiene	$\begin{array}{c} \text{---CH}_2 \quad \text{CH}_2 \text{---} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{CH=CH} \end{array} \left[\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{CH=CH} \end{array} \right]_x \begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \text{---} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{CH=CH} \end{array}$ <i>cis</i>-1,4-Polybutadiene
1,2-Polybutadiene	$\left[\begin{array}{c} \text{CH}_2 \text{---CH} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_2 \end{array} \right]_n$
<i>trans</i> -1,4-Polybutadiene	$\left[\begin{array}{c} \text{CH}_2 \\ \quad \quad \quad \\ \quad \quad \quad \text{CH=CH} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_2 \end{array} \right]_x$
Styrene-Butadiene	$\left[\begin{array}{ccccccc} & \text{H} & & \text{H}_2 & \text{H} & & \text{H}_1 \\ & & & & & & \\ \text{---C} & \text{---C} & \text{---C} & \text{---C} & \text{---C} & \text{---C} & \text{---} \\ & & & & & & \\ & \text{H}_1 & & \text{H} & & & \text{C}_6\text{H}_5 \end{array} \right]$
Acrylonitrile-Butadiene-	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{---C} & \text{---C} \text{---} \\ & \\ \text{H} & \text{CN} \end{array} \right]_a \quad \left[\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{---C} & \text{---C} & \text{---C} & \text{---C} \text{---} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array} \right]_b \quad \left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{---C} & \text{---C} \text{---} \\ & \\ \text{H} & \text{CH} \end{array} \right]_c$ Acrylonitrile Butadiene Styrene

problem in handling and storage. The rate of dimer formation is a function of temperature, as shown below (Exxon, 1974):

<u>temperature</u> (°C)	<u>wt % butadiene dimerized/hr</u>
20	0.00015
40	0.0014
60	0.013
80	0.12
100	1.1

At 46°C, about 1.6% of butadiene is dimerized after 30 days storage, but about 16% of butadiene is dimerized at 75°C after this period. Because of this, butadiene is usually stored at low temperatures (Exxon, 1974).

The dimerization reaction has been used commercially to prepare vinylcyclohexene by heating butadiene under pressure (Hillyer and Stallings, 1956):



Stahly (1951) reported improved yields using a metal naphthenate salt catalyst. Butadiene was heated in liquid phase at 150-160°C and 40-100 atmospheres for a few minutes in the presence of a metal naphthenate salt catalyst, to yield more than 60% vinylcyclohexene by weight of butadiene treated. Johnson (1949) prepared the dimer by heating butadiene in the vapor phase to 375-450°C in the presence of silicon carbide. Candlin and Janes (1968) reported high yields at 100°C using iron carbonyls. Other catalysts described in the patent literature include dicyclopentadienyl nickel and nickel dicarbonylphosphite complexes (Bailey, 1971). According to Tkatchenko

(1977) the most selective catalyst systems are based on cobalt, rhodium or platinum.

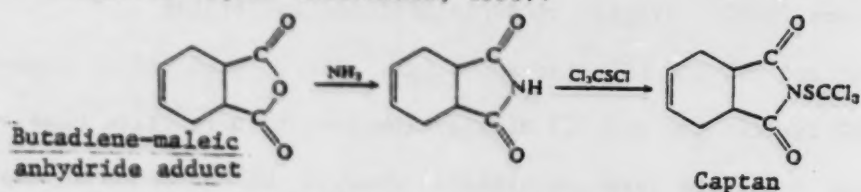
Besides six-membered rings formed by Diels-Alder reactions, butadiene also forms rings of other sizes. The cyclodimerization of butadiene results in 1,5-cyclooctadiene (COD). Ziegler prepared mixtures containing vinylcyclohexene and 15% COD (Ziegler and Wilms, 1947). Reed (1954) reported yields of 30-40% cis,cis COD and 10% vinylcyclohexene in a reaction time of 4 hours using Reppe catalysts based on nickel carbonyl. Wilke (1963) attempted to improve yields by further developing the nickel catalyst system. Nickel reduced in the presence of triphenylphosphine catalyzed cyclodimerization to yield a mixture of 70% COD, 10% cyclododecatriene and 20% vinylcyclohexene. A number of other nickel catalysts have been described; among them are nickel tetracarbonyl with tri-*o*-cresyl phosphite and also acrylonitrile and tri-*o*-tolyl phosphite (summarized in Baily, 1971). Thermal dimerization without catalysts will yield primarily cis,cis-cyclooctadiene, 4-vinylcyclohexene and trans-1,2-divinylcyclobutane (Huybrechts et al., 1977)

c. Trimerization to Cyclododecatriene

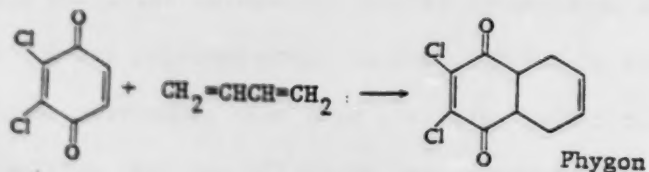
Trimerization of butadiene will yield cyclododecatriene (CDT) in the presence of metal-alkyl-transition metal catalysts. Wilke (1963) prepared CDT in a 90-95% yield from butadiene in the presence of a diethylaluminum hydride catalyst at 40°C and normal pressure. Other catalysts described by Wilke (1963) for obtaining high yields were prepared from calcium hydride, aluminum chloride in both benzene and titanium tetrachloride and from chromyl chloride and triethylaluminum in benzene. Several stereoisomers of cyclododecatriene are possible (Table 3); the products depend primarily on the catalyst system.

d. Diels-Alder Reaction with Other Adducts

In addition to dimerization, other Diels-Alder reactions are of commercial importance. Butadiene reacts urea maleic anhydride to form 1,2,5,6-tetrahydrophthalic anhydride (THPA) which is used in the preparation of the fungicide Captan (Kittleson, 1951):



Another commercial product based on a Diels-Alder reaction of butadiene is the insecticide Phygon (Kittleson, 1951):



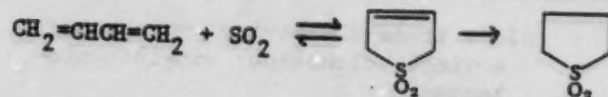
Also of use commercially is the reaction of butadiene and naphthalene in the production of anthraquinone (Weyker et al., 1960). There is a large literature on Diels-Alder dienophiles that react with butadiene but these are primarily of laboratory interest; Baily, (1971) lists over 300 dienophiles in his review of butadiene.

e. Other Reactions

Chlorination or hydrocyanation of butadiene is used in the manufacture of adiponitrile, an intermediate in the production of nylon 6,6 (See Section II-B-1-e). Butadiene is also chlorinated to make chloroprene (See II-B-1-c).

The reaction of butadiene and dihalocarbenes is used in the synthesis of vinyl dihalocyclopropanes. Hydrogenation of butadiene gives butenes and butane, the ratio depending on the catalyst used (Kirchenbaum and Kahn, 1964).

A cyclization reaction of industrial significance is the formation of sulfolane. Butadiene reacts with SO_2 under pressure to yield a cyclic sulfone, which yields tetramethylene sulfone on reduction:



Sulfolane is used as a solvent for aromatics extraction and purification of acid gas.

f. Photochemistry

The photochemistry of butadiene is quite complex. It can be made to decompose via one of 5 primary processes or to dimerize in one of four ways, depending on whether the photolysis is carried out in the gas phase or in solution, and whether sensitization or direct absorption is involved (Table 7). Some of the resulting products undergo secondary photolysis (Srinivason, 1966).

The dimerization of butadiene has been studied in the liquid phase, mostly by irradiation in the presence of photosensitizers (carbonyl compounds that excite butadiene to the lowest triplet state). Three products are formed: i) cis-divinylcyclobutane, ii) trans-divinylcyclobutane and, iii) vinylcyclohexene. The proportion of products formed depends on the sensitizer used, as shown in Table 8 (Liu et al., 1965; Hammond et al., 1961, 1963).

The direct irradiation of 253.7 nm solutions of butadiene (i.e., no photosensitizer) results in less than 10% conversion to dimers. The dimers obtained, in order of decreasing yield, are: 2-vinylbicyclo-hexane; 1,2-divinylcyclobutane; 1,5-cyclooctadiene; and an unidentified dimer (Srinivasan and Sonntag, 1965).

Table 7
Products of Photochemical Reactions
of Butadiene (Srinivason, 1966)

Type of reaction	Primary products	Phase in which observed
Dimerization	cis-, trans-1,2-divinylcyclobutane; 4-vinylcyclohexene; vinylbicyclo- hexane	Solution
Valence tautomerization	Bicyclobutane, cyclobutene	Solution
Hydrogen migration	C ₂ H ₂ and C ₂ H ₄ , 1,2-butadiene	Vapor
Dehydrogenation	H ₂ + vinylacetylene	Vapor

Table 8
Composition of Products from Photosensitized
Dimerization of Butadiene^a (Liu et al., 1965)

Sensitizer ^b	Percentage distribution of dimers		
	trans-1,2- Divinyl- cyclo- butane	cis-1,2- Divinyl- cyclo- butane	4- Vinyl- cyclo- hexene
Benzaldehyde	80	16	4
Anthraquinone	77	19	4
β-Naphthaldehyde	71	17	12
Fluorenone	44	13	43
Pyrene	~30	~10	~60
Eosine	60	17	23

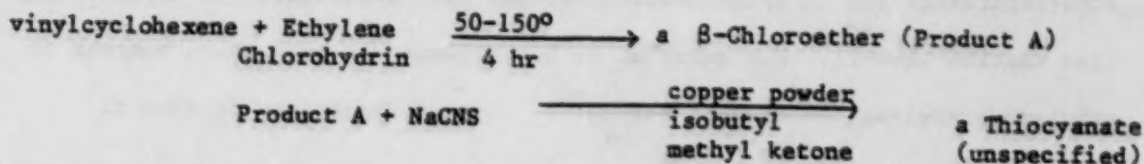
^a 28 sensitizers listed in original reference.

^b Sensitizer was 0.1 M in ether.

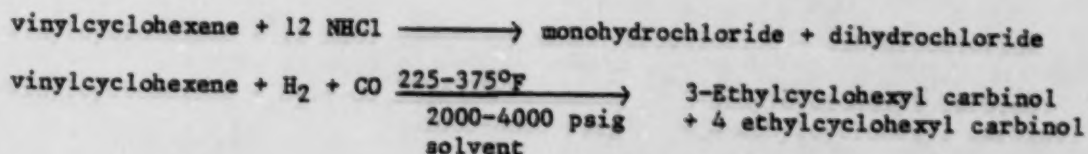
When butadiene is irradiated (253.7 nm) in a dilute solution, a mixture of bicyclobutane and cyclobutene is formed by a valence tautomerization reaction. When irradiation is carried out in the vapor phase, several reaction products form as a result of hydrogen migration and dehydrogenation, including hydrogen and possibly vinylacetylene (Srinivasan, 1966).

2. Oligomers

Typical industrial reactions of butadiene oligomers have been discussed in Citco (1969) and Bengelsdorf et al. (1960) and are summarized below. Company product bulletins list several uses of vinylcyclohexene, such as in preparation of some insecticidal preparations:



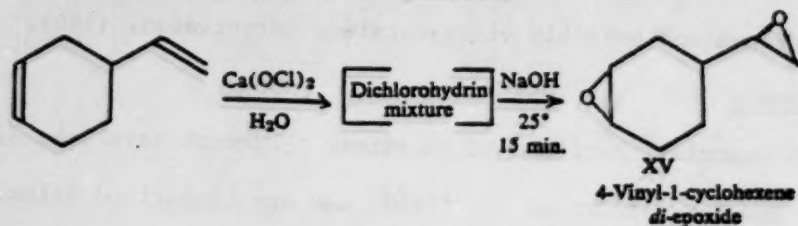
The products of the following reactions of vinylcyclohexene are used in or as plasticizers:



Vinylcyclohexene can be oxidized to produce tricarboxylic acids. The OXO reaction produces a ten-carbon diacid, dialdehyde or diol. It is a useful intermediate in preparing aromatic compounds from aliphatic hydrocarbons because it can be easily dehydrogenated to an aromatic derivative (Stanley, 1951).

Products useful as anti-oxidants are formed from the reaction of vinylcyclohexene and resinous condensate $((\text{CH}_3)_2\text{CO}-(\text{C}_6\text{H}_5)_2\text{NH})$. Vinylcyclohexene is used to prepare 4-vinyl-1-cyclohexene di-epoxide which is

further used in the manufacture of polyesters, coatings or hard, clear plastics. The di-epoxide can be formed during a two step process whereby vinylcyclohexene is treated with calcium hypochlorite and the resulting dichlorohydrin mixture is dehydrohalogenated:



Cyclooctadiene and cyclododecatriene are produced from butadiene (see section II-A-1-b). These oligomers are used as raw materials in fire-retardants and in nylon production, and have other possible applications (See section II-B-2). For example, cyclooctadiene may be a third monomer in ethylene-propylene terpolymer (NordelTM). Cyclododecatriene is used to produce a feedstock for nylon 12.

II. ENVIRONMENTAL EXPOSURE FACTORS

Aspects of commercial production, use, environmental contamination and degradation are considered in the following sections. The discussion is primarily on butadiene, as little information is available for the oligomers on these topics.

A. Production Processes

1. Production

a. Butadiene

In the United States three main routes are used commercially to obtain butadiene from refinery streams. Two are dehydrogenation processes; via either n-butane or n-butene. The third route is as a co-product of ethylene manufacture. All processes require final recovery of butadiene by extractive distillation. Table 9 shows the process and recovery systems currently used by the domestic butadiene producers. During 1977, the ratio of dehydrogenation to coproduct butadiene was 45:55 (Anon, 1978a). There is a trend, however, to phase out dehydrogenation in favor of co-product capacity (Section II-A-6).

1) Houdry Process: Dehydrogenation of n-Butane

Normal butane can be catalytically dehydrogenated to butadiene. In the widely-used Houdry Process (Table 9) dehydrogenation is accomplished in one step over a chromia-alumina catalyst. The feed can be any complex mixture of hydrocarbons (Baily, 1971); a typical butane stream and yield are shown in Table 10. The feed is preheated to 620°C and then passed to a series of fixed-bed reactors containing shallow beds of the catalyst held at 600-620°C and 150 mm Hg absolute pressure (Figure 2). The first reactor is on-line for about 5-10 minutes. The feed is then passed to the next reactor so that the

Table 9
1,3-Butadiene Producers in the United States
(Anon, 1977a; Erickson, 1977; Anon., 1976a
Amoco, 1978; Firestone, 1978; Texas U.S., 1978)
A. Butadiene by Dehydrogenation

Company	Process	Recovery System	Capacity (millions of pounds/yr.)
Arco Chemical Channelview, Tx.	Houdry Catadiene	Phillips Furfural	140
Copolymer Rubber & Chem.	Petro-Tex Oxid. Dehydrog.	Exxon Cuprous Ammonium Acetate	160
Baton Rouge, La.			
El Paso Products Odessa, Tx.	Houdry Catadiene	Exxon Cuprous Ammonium Acetate	205
Firestone Orange, Tx.	Houdry Catadiene	Shell Acetonitrile, Exxon Cupious Ammonium Acetate Exxon Cupious Ammonium Acetate	248
B.F. Goodrich Chem. Port Neches, Tx.	Petro-Tex. Oxid. Dehydrog. Dow Catalyst Petro-Tex Oxid. Dehydrog.	Phillips Furfural Phillips Furfural	360
Petro-Tex Chemical Pasadena, Tx.	(Houdry Catadiene Petro-Tex Oxid. Dehydrog.	Phillips Furfural) ^b Phillips Furfural	880

^a Feed, process and recovery system data primarily from Erickson, 1977.

^b Shut down in January, 1977; these units will be converted to by-product extraction equipment (Anon, 1976b).

Table 9 (Con't)

1,3-Butadiene Producers in the United States
(Anon, 1977a; Erickson, 1977; Anon., 1976a
Amoco, 1978; Firestone, 1978; Texas U.S., 1978)

Company	Process	Recovery System	Capacity (millions of pounds/yr.)
Phillips Petroleum Borger, Tx.	(Phillips Butane to Butylene Dehydrog. Phillips Oxid. Dehydrog.	Phillips Furfural) ^d Phillips Furfural	310
Texas-U.S. Chemical ^c Port Neches, Tx.	Dow Catalyst Process Petro-Tex Oxid. Dehydrog.	Phillips Furfural	250
B. Extraction Processes			
Company	Process	Recovery System	Capacity (millions of pounds/yr.)
Arco Chemical Channelview, Tx.	-	-	260
AMOCO Chemicals Alvin, Tx.	Shell Acetonitrile	-	190
Corpus Christi Petrochem. Co. Corpus Christi, Tx.	-	-	-e
Dow Chemical Freeport, Tx. Plaquemine, La.	Shell Acetonitrile	-	135

^c Joint owner of Neches Butane Products with B. F. Goodrich.

^d Plants shut down according to Green & Pennington, 1977.

^e On stream in late 1979, early 1980 (Anon., 1977b).

^f New olefin plant to come on stream by 1980, adding 250 million pounds to Exxon capacity (Anon., 1977a).

Table 9 (Con't)
1,3-Butadiene Producers in the United States
(Anon, 1977a; Erickson, 1977; Anon., 1976a,
Amoco, 1978; Firestone, 1978; Texas U.S., 1978)

Company	Recovery System	(millions of pounds/yr)
Exxon Chemical Baton Rouge, La.	Exxon cuprous ammonium acetate Nippon Zeon dimethyl formamide system	340 ^f
Mobil Chemical Beaumont, Tx.	Phillips Furfural	80
Monsanto Co. Chocolate Bayou, Tx.	Monsanto Furfural - methoxypropionitrile	120
Neches Butane Products ^g Port Neches, Tx.	-	360
Puerto Rico Olefins Ponce, P.R.	Shell Acetonitrile	210
Shell Chemical Deer Park, Tx.	Shell Acetonitrile	280
Union Carbide Penueles, P.R. Seadrift, Tx. Taft, La. Texas City, Tx.		315 (150) (45) (65) (55)

^f New olefin plant to come on stream by 1980, adding 250 million pounds to Exxon capacity (Anon., 1977a).
^g Facility jointly owned by Texas-U.S. and B. F. Goodrich.
^h By mid 1978, Shell will add 90 million lbs. to capacity; additional capacity of 250 million lbs. expected by 1979 (Anon., 1977a). A unit will be built in Norco, La. to recover 500 million lb./year (Anon., 1977c).

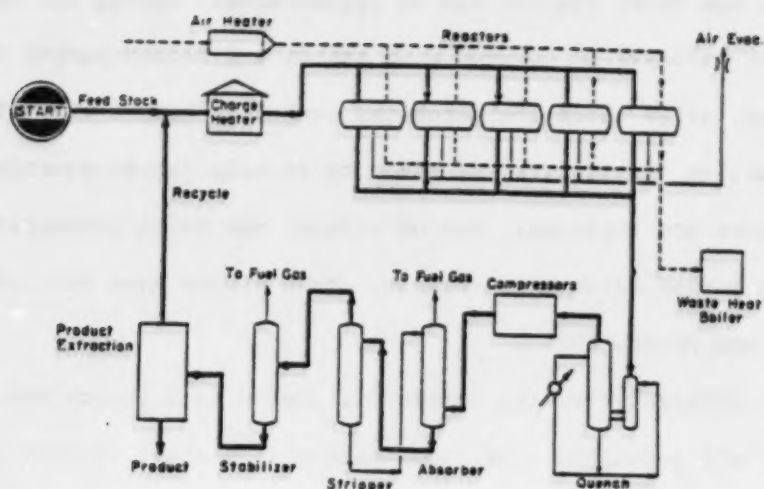


Figure 2. Houdry Process for the Dehydrogenation of n-Butane (Anon., 1971)
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Table 10
Typical Ultimate Yields of
Butadiene from a Normal
Butane Feed Stream (Houdry
Process) (Anon., 1971)

Component	Feed (% by weight)	Net Products (% of fresh feed)		
		Butadiene	Fuel Gas ^a	Unrecovered
Dry Gas	-	-	16.3	-
Isobutane	1.0	-	-	-
Isobutylene	-	-	0.5	-
n-Butylenes	-	0.3	2.5	-
n-Butane	99.0	-	1.8	-
Butadiene	-	64.4	0.6	-
C ₅ , Coke, C and H ₂ to CO, CO ₂ and H ₂ O	-	-	1.6	12

^a Butane-butylene fraction may be used in fuel gas manufacture.

catalyst in the first reactor can be regenerated. During the regeneration process, the catalyst is covered with carbon and vacuum-purged to remove hydrocarbons, after which the deposited carbon is burned-off. The catalyst is then at reaction temperature and ready to sustain dehydrogenation. At least three reactors are required: one on stream, one being regenerated, and one being steam purged after regeneration. Most plants have five or more reactors (Lowenheim and Moran, 1975).

The hot effluent from the reactor is cooled in a quench tower, stripped of heavy materials and light ends, then passed to a stabilization system. The stabilized product stream is now ready for product extraction (Subsection a-4). Some butylenes are formed which may either be recycled to the reactor or used in aviation gasoline manufacture (Lowenheim and Moran, 1975; Anon, 1971).

2) Oxidative Dehydrogenation: Dehydrogenation of n-Butene

Another dehydrogenation process is one which uses normal butenes rather than normal butane. This process, referred to as oxidative dehydrogenation, oxydehydrogenation or OXD, was commercialized by Petro-Tex in 1965 and is in use at production sites listed in Table 9A. The advantage of this process is the savings in fuel; OXD is an exothermic rather than an endothermic process and therefore, uses less energy than other dehydrogenation processes.

Hutson et al. (1974) described the process used by the Phillips Petroleum Co. Steam, air, and normal butenes are introduced into the OXD reactor and then passed over a fixed catalyst bed at 900-1100°F (482-593°C). As butenes are dehydrogenated, the hydrogen that is released forms water, after reacting with oxygen in the air. Removal of hydrogen from the reaction environment permits the dehydrogenation reaction to proceed to a greater extent than in ordinary dehydrogenation. The catalyst is regenerated in situ in the presence of steam and air in the reactor. Phillips reported

per-pass butadiene yields in a pilot plant of 70%.

Catalytic dehydrogenation of butenes was used until several years ago, but now dehydrogenation plants employ an oxidative dehydrogenating agent.

3) Co-Product in Ethylene Production

The production of ethylene from the cracking of hydrocarbons (e.g. naptha, ethane, propane, gas oil etc.) results in C_4 streams from which butadiene can be extracted.

Figure 3 shows a typical process for producing ethylene. The hydrocarbon feedstock is pre-heated and cracked in the presence of steam; the resulting product is passed to the pyrolysis/quench system. From the quench system, the raw gas is compressed; carbon dioxide and hydrogen sulfide are removed. The stream is then passed through a series of fractionators (Anon., 1977d) with the mixed C_4 stream being recovered. The amount of butadiene that can be extracted depends particularly on the hydrocarbon feedstock used (Table 11) and on the cracking operation. The recovery processes used are listed in Table 9 and described in the next section.

Table 11
Average Yield of By-Product
Butadiene From Ethylene
Feedstocks (Lowenheim and Moran, 1975)

Ethylene Feedstock	By-Product Butadiene Yield (kg/100 kg ethylene produced)
Ethane	2.5
Propane	7.1
Butane	8.7
Medium-Range Naptha	13.6
Atmospheric Gas Oil	17.6
Light Vacuum Gas Oil	24.7

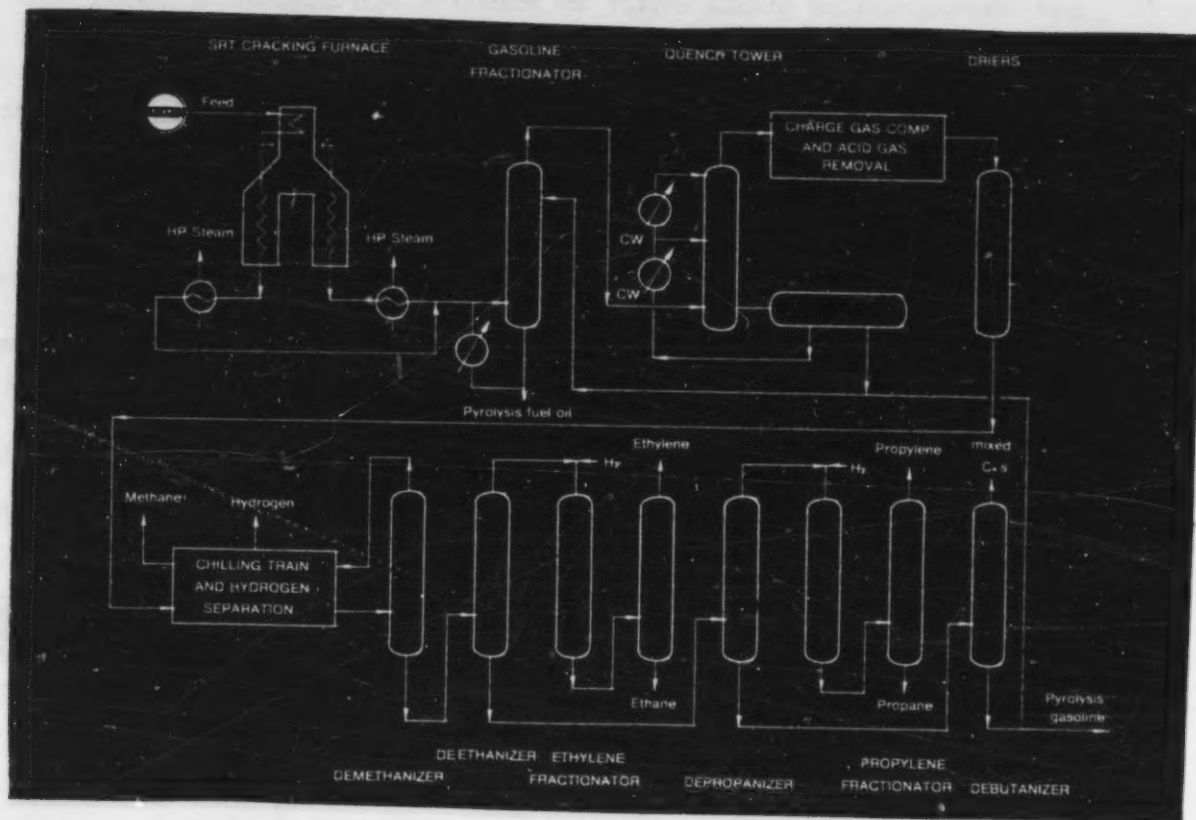


Figure 3. A Process for the Production of Ethylene (Anon., 1977d)
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Texas

4) Extractive Distillation

In the 3 commercial processes just described (dehydrogenation of n-butane; dehydrogenation of n-butene; co-product of ethylene manufacture) butadiene must be isolated from other hydrocarbons in the product mixture. This cannot be accomplished by simple distillation because the boiling points of other C_4 hydrocarbons in the mixtures are very close to that of butadiene. Extractive distillation is often employed, and involves the use of a polar solvent to change the relative volatility of the components being distilled. Widely used solvents are furfural and acetonitrile, in processes developed by Phillips Petroleum Co. and Shell Chemical, respectively. Other recovery processes in use are Exxon's Cuprous Ammonium Acetate System, Nippon Zeon's Dimethyl Formamide System and Monsanto's Furfural-Methoxypropionitrile System (Table 9).

A flow chart for Phillip's Furfural Separation System for butadiene extraction is shown in Figure 4 (Peters and Rogers, 1968). In this process C_4 from an ethylene plant and furfural are fed into the extractive distillation tower. Heat is then supplied at the base of the tower and the overhead product is withdrawn (primarily butanes, butenes, allene, methyl acetylene and light weight hydrocarbons). A solvent-butadiene mixture, C_4 acetylenes and 2-butenes are withdrawn from the bottom and fed to a stripper tower where C_4 components are removed. The product is then sent to a conventional distillation tower where 2-butene, C_4 acetylenes, 1,2-butadiene and carbonyls are withdrawn from the base; high-purity 1,3-butadiene is removed overhead (Peters and Rogers, 1968).

b. Oligomers

Small quantities of vinylcyclohexene, cyclododecatriene and cyclooctadiene are produced commercially from butadiene.

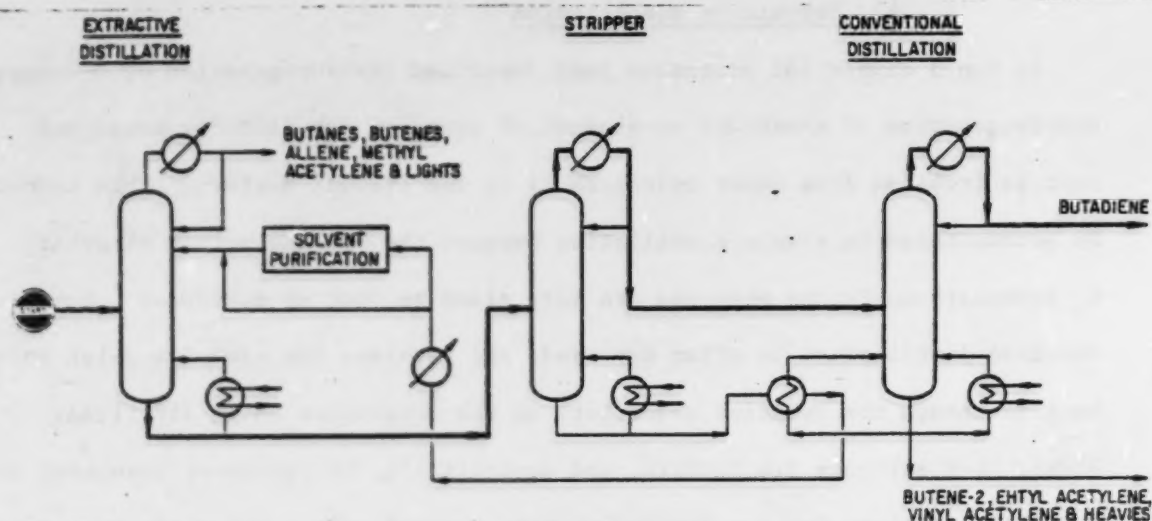


Figure 4. Phillip's Furfural Extraction Process for Butadiene (Peters and Rogers, 1968). Reprinted by Permission from Gulf Publishing Co., Houston, Texas

Vinylcyclohexene is produced as a byproduct of either butadiene or cyclooctadiene/cyclododecatriene manufacture (Henderson, pers. comm., 1978). The dimerization reaction of butadiene to form vinylcyclohexene is discussed in section I-D-1-b).

Butadiene is selectively dimerized to cyclooctadiene and trimerized to cyclododecatriene. Conventionally, Ziegler catalysts or organo nickel complexes have been used. Ono and Kihara (1967) reported that several new catalysts have been developed in Japan: bisacrylonitrile nickel to produce cyclododecatriene and bisacrylonitrile nickel-triphenyl phosphine or tetraphenylisonitrile nickel-triphenyl phosphite to produce cyclooctadiene or mixtures of cyclooctadiene and cyclododecatriene (Figure 5). Butadiene, a non-polar solvent, and the catalyst are introduced into the reactor which is held at 80°C and a maximum pressure of 10 kg/cm². After the reaction, the product solution undergoes successive recovery processes for the separation of unreacted butadiene, solvent, by-products and vinylcyclohexene. After this,

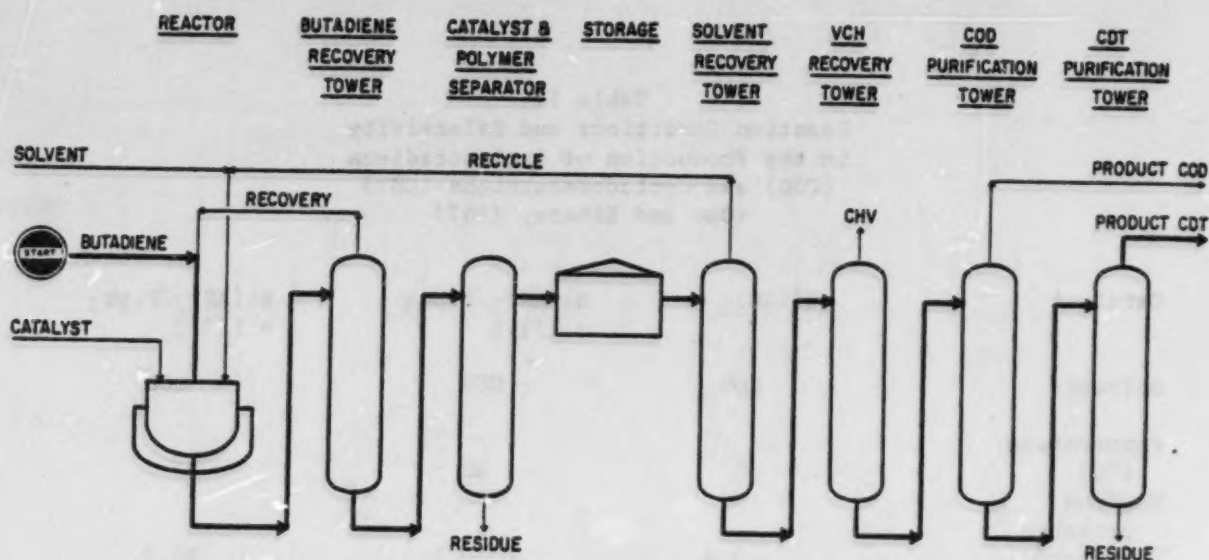


Figure 5. Toyo Soda (Japan) Process for Cyclooctadiene and Cyclododecatriene Manufacture (Ono and Kihara, 1967). Reprinted by Permission from Gulf Publishing Co., Houston, Texas

cyclooctadiene and cyclododecatriene are purified and then recovered. The ratio of cyclooctadiene to cyclododecatriene produced depends on the catalyst used (Table 12). With the 3 catalysts described by Ono and Kihara (1967), the cyclododecatriene produced is predominantly the trans, trans, trans-isomer (Ziegler type catalysts produce mainly the trans, trans, cis-isomer).

Morikawa et al. (1972) described a process for producing cyclododecatriene using a mixed C_4 stream rather than pure butadiene as a starting material. The C_4 stream may contain as much as 35 wt.-% butadiene. Per-pass yields range from 75 to 80% of maximum for cyclododecatriene. In this process, butadiene is cyclotrimerized to form 3 isomers of cyclododecatriene, the configuration produced being dependent on the catalyst composition. Cyclododecatriene is then hydrated to cyclododecane used to make nylon-12, a polyamide plastic. As in the process described by Ono and Kihara (1967) an unwanted side reaction is the formation of vinylcyclohexene, which can, however, be removed by distillation.

Table 12
Reaction Conditions and Selectivity
in the Production of Cyclooctadiene
(COD) and Cyclododecatriene (CDT)
(Ono and Kihara, 1967)

Catalyst	Ni(AN) ₂	Ni(AN) ₂ /P.ph ₃ = 1/1.6	Ni(AN) ₂ /P.ph ₃ = 1/3.2
Solvent	COD	COD	COD
Temperature (°C)	80	80	80
Maximum pressure (kg/cm ²)	9.8	10.3	10.3
Conversion (%)	96.5	94.5	95.4
Selectivities (%)			
VCH	6.0	6.2	6.5
COD	7.1	53.9	84.9
CDT	80.4	35.2	4.5
Lights	1.1	0.9	0.7
Heavies	5.4	3.8	3.4

AN = acrylonitrile
ph = phenyl

2. Quantity Produced

Butadiene ranks 30th in a list of all chemicals with respect to quantity produced (U.S. Int. Tariff Comm., 1976). During the first quarter of 1978 production of butadiene was at 82% of name-plate capacity (4.3 billion pounds/year) or at 91% of effective (practical maximum) capacity (Anon., 1978b). U.S. production of butadiene during 1978 is predicted to be 3.3 billion pounds, up about 6% from 1977 (Anon., 1977e). U.S. butadiene is about 40% of worldwide production (8.8 billion pounds) (Anon., 1978a).

The U.S. International Trade Commission reports production figures for rubber-grade butadiene and for butadiene and butylene fractions. As shown in Table 13 A, production of rubber-grade butadiene steadily increased during the last decade until 1975, when a sharp decrease occurred as part of the general economic recession. Production recovered during 1976 but not as much as forecasted for two reasons: i) the U.S. rubber strike and ii) steam cracking operations produced less coproduct butadiene than expected (Anon., 1976b). Data for butadiene and butylene fractions appear in Table 13 B; butadiene from this source is presumably used in non-rubber applications. The U.S. International Trade Commission does not list production figures for butadiene oligomers.

3. Domestic Producers and Production Sites

There are 8 domestic producers of 1,3-butadiene using dehydrogenation processes (Table 9 A) and 8 different producers using extraction processes (Table 9 B). Total dehydrogenation capacity is about 2.6 billion pounds, with Phillips and Petro-Tex being the largest producers. Extraction capacity is currently 2.3 billion pounds, lead by Exxon and Neches Butane. Summing both processes, total butadiene capacity is about 4.90 billion pounds from 20 production sites: 14 in Texas, 4 in Louisiana and 2 in Puerto Rico (Table 9).

Table 13
U.S. Production and Sales of Butadiene:
A) Rubber-Grade Butadiene and B) Butadiene and
Butylene Fractions^a

	Production (million lbs.)	Sales (million lbs.)	Value of Sales (1,000 \$)	Average Cost, Cents/Pound
A) Rubber-Grade Butadiene				
1977 ^b	3,187			
1976	3,507.3	2,188.7	387,018	17.6
1975	2,597.0	1,887.3	310,574	16.5
1974	3,682.1	2,500.8	363,932	14.6
1973	3,643.5	2,416.5	196,552	8.1
1972	3,527.4	2,230.0	173,844	7.8
1971	3,340.3	2,022.6	167,274	8.3
1970	3,101.4	1,947.2	163,967	8.4
1969	3,123.0	1,981.9	167,312	8.4
1968	2,928.7	1,942.6	171,917	8.8
1967	2,660.3	1,620.8	154,266	9.5
B) Butadiene and Butylene Fractions				
1976	1,398.7	406.7	35,670	8.7
1975	756.2	284.8	29,408	10.3
1974	757.7	362.1	21,337	5.9
1973	535.2	450.3	12,310	2.7
1972	568.0	436.2	11,817	2.7
1971	687.2	429.8	11,808	2.7
1970	743.5	409.3	12,846	3.1
1969	1,264.2	280.4	8,281	3.0
1968	1,042.9	245.4	7,217	2.9
1967	894.2	238.6	6,997	2.9

^aSource: U.S. Int. Trade Comm. 1973-1977
U.S. Tariff Comm. 1967-1972

^bPreliminary

Crude vinylcyclohexene used to be offered for sale on an "as is" basis by Texas-U.S. Chemical Company (i.e., no sales specifications); the customer could use the material as it was or redistill it. Due to a limited market and captive needs, Texas U.S. no longer offers it in the merchant market (Rodde, pers. comm., 1978); vinylcyclohexene is not made intentionally. CTC Organics (Atlanta, Ga.) offers it for sale on an "as-needed" basis; they purchase crude byproduct stream and purify it (Liu, pers. comm., 1978). Also, Cities Service Co. offers 97% pure vinylcyclohexene as a byproduct of butadiene or cyclo-octadiene/cyclododecatriene manufacture (Henderson, pers. comm., 1978). Purified (99%) vinylcyclohexene can be purchased from the Aldrich Chemical Co. in 500 g or 2 kg quantities.

Cyclooctadiene is manufactured by the Cities Service Co., Inc. (Lake Charles, La.). The annual capacity is 25 million pounds; however, actual production figures are unavailable (Henderson, pers. comm., 1978). Cyclododecatriene can also be produced by Cities Service at the Lake Charles Plant, but DuPont is currently the only cyclododecatriene producer in the U.S. (Henderson, pers. comm., 1978). DuPont's cyclododecatriene is used captively and no up-to-date capacity figures have been published. In 1972, DuPont's capacity for cyclododecatriene was rated at 2.2 million pounds, but the plant has since expanded (Simpson, pers. comm., 1978; Anon., 1972).

4. Foreign Importers and Producers

Imports of 1,3-butadiene into the U.S. totalled 595 million pounds during 1976 and came primarily from the Netherlands (42.3%) and the United Kingdom (22%), with smaller amounts from Belgium, France, Italy, Japan and West Germany (Table 14; U.S. Bureau of the Census, 1976). Imports have increased more than 65% from 1972 levels. Since that time Canada, Finland and Mexico also exported small amounts of butadiene into the United States (Table 14; U.S.

Table 14
Imports of Butadiene^a into the United States^b

	1976	1975	1974	1973	1972
Total Quantity Gallons	113,910,892	107,305,733	114,593,177	70,112,451	68,052,945
Pounds ^c	595,640,005	561,101,677	599,207,722	366,618,006	355,848,849
Country of Origin (%)					
Belgium	1.6	-	1.3	-	-
Canada	-	1.9	0.2	4.9	11.4
Finland	-	1.0	-	-	-
France	10.7	13.6	18.9	12.6	3.5
Italy	8.8	4.5	4.9	9.2	2.6
Japan	10.5	27.2	24.6	35.3	59.6
Mexico	-	3.0	-	-	-
Netherlands	42.3	33.1	43.0	32.3	17.7
U. Kingdom	22.0	10.7	5.3	3.0	5.2
W. Germany	4.1	5.0	1.8	2.7	-

^a Commodity number 4295020.

^b Source: U.S. Bureau of Census 1972-1976.

^c Using conversion factor 1 gallon = 5.229 lbs. (At 60°F).

Bureau of the Census, 1972-1976). Ericksson (1976) expects imports to increase from now until the early 1980's. Producers such as Exxon, Shell and Arco expect butadiene imports to increase to 1 billion pounds or more by the early 1980's (Prescott, 1976). However, Debreczeni (1977) forecasts imports to remain at about 500 million pounds through 1990. He predicts imports will represent a slowly decreasing percentage of total U.S. butadiene supply (12% 1977; 8% 1990) as domestic extraction capacities are increased (Table 15).

In Western Europe all butadiene capacity is by extraction (Driver, 1976). Current butadiene capacities and production figures for several European countries appear in Table 16. The annual rate of growth for butadiene production in these countries is expected to be about 8.2% per year (Klaus, 1977). P. N. Collinswood of B. P. Chemicals Ltd. predicts a potential growth surplus of butadiene in Europe of almost 750,000 tons/year by 1990, up considerably from levels in 1974-1975 (250,000 tons/year). He forecasts that outlets for this European surplus will not exist by about 1985 (Anon., 1977f).

The U.S. Bureau of the Census does not list import data for butadiene oligomers. Major European manufacturers of cyclooctadiene and/or cyclododecatriene are Huls (cyclododecatriene capacity of 26 million pounds) and Shell Chemie (Berre, France; cyclododecatriene/cyclooctadiene capacity of 22 million pounds) (Anon., 1972).

5. Market Price

In January 1978 the market price of butadiene ranged from 20.5 to 22.75 cents per pound (f.o.b., Gulf Coast) (Petro-Tex Chem. Corp., 1978), up from 18.25-18.5 cents per pound quoted during early 1977 (Anon., 1977g). According to Ericsson Chemical Services (Anon., 1977h), recent price increases reflect: i) increased domestic demand for butadiene, ii) reduced operating rates for European and Japanese ethylene plants and iii) the shut-down by Petro-Tex of

Table 15
Butadiene Supply in the United States (Debreczeni, 1977)^a

	Billions of Pounds			
	1977	1980	1985	1990
Extraction by Ethylene Producers	1.2 (29%) ^b	1.5 (34%)	2.1 (42%)	2.8 (45%)
Extraction by Butadiene Producers	0.6 (14%)	1.1 (25%)	1.9 (38%)	2.1 (40%)
Dehydrogenation of Butane and/or Butylene	1.9 (45%)	1.3 (30%)	0.5 (10%)	0.2 (4%)
Imports	0.5 (12%)	0.5 (11%)	0.5 (10%)	0.5 (8%)
Total	4.2	4.4	5.0	5.2
				6.2

^a Data in bar graphs in original reference.

^b Percent of total supply.

Table 16
European Butadiene Capacity and Production
for 1978 (Klaus, 1977)

Country	1978 Estimated Effective Capacity (Millions of pounds) ^a	1978 Estimated Production (Millions of pounds) ^a
Belgium, Netherlands, and Luxembourg	1124	849
Federal Republic of Germany	1356	1158
France	794	662
Italy	540	443
United Kingdom	838	617
Spain	198	198

^a Original units in metric tons.

more than half of their butadiene facility.

Debreczeni (1977) predicts that the price of butadiene will remain high enough to keep dehydrogenation plants operating until demand can be satisfied from extraction units. That is, if the price of either imported or extraction butadiene falls below the "breakeven" point of dehydrogenation, the dehydro producer could be forced to close. Debreczeni further forecasts that when sufficient coproduced butadiene becomes available (perhaps by 1987) the price of butadiene will likely decrease but concomitant increases in the price of ethylene and/or propylene can be expected.

Historically, the average price of butadiene increased in the U.S. from 8.4 in 1969 to 14.6 cents per pound in 1974 (Table 13). Driver (1976) analyzed butadiene pricing in Western Europe for that time period and concluded that these increases reflected the performance of butadiene derivatives rather than changes in the cost of production and extraction. That is, the upper limit on the price of butadiene is determined by what the major derivatives can bear before their competitive position in their own markets is threatened. For example, as the price of styrene-butadiene rubber (SBR) increased, so did the price of butadiene.

Cyclooctadiene, vinylcyclohexene and cyclododecatriene are available from Citco in 1 and 5 gallon cans for \$1.00 per pound. The first two compounds are also available at the same price in drum quantities (400 pounds/drum). Lower prices are quoted for cyclooctadiene for truckload drum, (\$0.85/lb., minimum 20,000 lbs.) and tank truck (\$0.75/lb.; minimum 30,000 lbs.) quantities (Citco, 1977).

6. Market Trends

The average annual growth of butadiene has been about 2% during the period from 1967-1976. Future growth of 4% per year is forecasted through 1981 (Anon., 1977a) when butadiene demand will reach 4.5 billion pounds (Greene and

Pemington, 1977)). Butadiene's future will depend particularly on basic tire rubbers, since about 85% of its consumption goes into tires and other rubber products. Forecasted butadiene demand for end-products are discussed in the next section and summarized in Table 17.

The supply or sources of butadiene will continue to reflect increasing co-product capacity. During the 1960's all domestic butadiene was produced by the dehydrogenation of butane and/or of butylenes. By 1970, 80% of production was via dehydrogenation, but this had decreased to about 50% by 1977 as supplies from co-product streams have increased (Table 15). The percentage of co-product butadiene supply available by 1985 has been forecasted between 80% (Debreczeni, 1977) and 67% (Ericksson, 1977). Total phase-out of dehydro capacity is predicted by 1990 (Table 15). Factors underlying this phase out are the economic and efficiency advantages of extraction. According to Ericcson (1976), this decrease does not mean a closing of dehydro units but rather, a conversion to extraction capacity. The extraction equipment at dehydro plants will be converted to recover butadiene from crude C_4 hydrocarbon streams brought from steam crackers.

The type of ethylene feedstock used is an important factor in co-product availability. As discussed (section 1-a-3) lower butadiene yields are obtained from ethane, propane or butane feedstocks than from naptha or gas oil. Indi- cations are for a growing importance of heavy feedstocks in ethylene manufac- ture. Of 14 announced ethylene plants or expansions, most (85%) will be based on heavy feeds. Thus, more coproduced butadiene will be available (Greene and Pennington, 1977).

B. Use

1. Butadiene

The major uses of butadiene include styrene-butadiene rubber (53%), polybutadiene rubber (18%), neoprene (7%), nitrile rubber (3%), adiponitrile (8%),

Table 17
Butadiene Demand in the United States
(Debreczeni, 1977)^a

	Billions of Pounds			
	1977	1980	1985	1990
SBR & SBR Latex	2.0 (48%) ^b	2.0 (46%)	2.1 (42%)	2.3 (39%)
Polybutadiene Elastomer	0.8 (19%)	0.8 (18%)	0.9 (18%)	1.0 (18%)
Nitrile & Polyisoprene Elastomers	0.6 (14%)	0.8 (18%)	0.9 (18%)	1.0 (18%)
Nylon 66 & other Chemicals	0.7 (17%)	0.7 (16%)	1.0 (20%)	1.2 (21%)
Miscellaneous & Exports	0.1 (2%)	0.1 (2%)	0.1 (2%)	0.2 (3.5%)
Total	4.2	4.4	5.0	5.7

^a Data in bar graphs in original reference.

^b percent of total demand.

acrylonitrile-butadiene-styrene resins (6%) as well as miscellaneous uses (5%) (Anon., 1977a). The uses and produces of these products (Table 18) are discussed in the sections which follow.

a. Styrene-Butadiene Copolymers

The largest use of butadiene is in the production of styrene-butadiene rubber (SBR) and latex, accounting for 53% of domestic butadiene demand (2.12 billion lbs/year) (Anon., 1977a). One type of SBR is used in tires (68% of total use). Other uses of SBR include: molded and extruded goods (13%), sponges (4%), footwear (3%) and miscellaneous uses (12%) such as foam rubber products and carpet backing (Anon., 1977i; Ericksson, 1977).

SBR is produced by solution and emulsion polymerization; the ratio of butadiene to styrene is generally 77:23 (Uranek, 1968). A typical emulsion SBR process is shown in Figure 6. There are several hundred types of SBR, depending on details of the process; 2 major categories are "hot SBR" and "cold SBR" referring particularly to polymerization temperatures of 60°C and 5°C, respectively. A typical formulation for cold SBR is given below (Saltman, 1965):

Typical Formulation for a "Cold" SBR

	Parts by Weight
Butadiene	72
Styrene	28
tert-dodecyl mercaptan	0.2
diisopropylbenzene monohydroperoxide	0.08
ferrous sulfate	0.14
potassium pyrophosphate	0.18
rosin acid soap	4.0
water	180

(polymerization goes to 60% conversion at 5°C after 12 hours)

Table 18
Producers and Capacities for Major Products
Using Butadiene

Producer	Capacity (Millions of lbs./year)	Reference
Styrene-butadiene Rubber^a		
American Synthetic Rubber, Louisville, Ky.	276	Anon., 1977i
Ashland, Baytown, Tex.	132	
Copolymer, Baton Rouge, La.	276	
Firestone, Lake Charles, La.	772	
Orange, Tex.	100	
General Tire, Odessa, Tex.	212	Anon., 1976c
B. F. Goodrich, Port Neches, Tex.	320	
Goodyear, Houston, Tex.	867	
Phillips, Borger, Tex.	275	
Texas-US, Port Neches, Tex.	399	
TOTAL	3629	
Polybutadiene Rubber^b		
American Synthetic, Louisville, Ky.	168	Anon., 1976d
Firestone, Orange, Tex.	230	
Goodrich, Orange, Tex.	134	
Goodyear, Beaumont, Tex.	246	
Phillips, Borger, Tex.	146	
TOTAL	924	
Neoprene		
DuPont, La Place, La.	80	Anon., 1976d
DuPont, Louisville, Ky.	300	
Petro-Tex, Houston, Tex.	66	
TOTAL	440	

^a Dry SBR; some capacity figures include carbon black and extender oils.
^b Net rubber basis of solution polymerized polybutadiene.

Table 18 (Cont.)
Producers and Capacities for Major Products
Using Butadiene

Producer	Capacity (Millions of lbs./year)	Reference
Nitrile Rubber^c		
Gopolymer, Baton Rouge, La.	11	Anon., 1976e
Firestone, Akron, Ohio	11	
Goodrich, Akron, Ohio	31	
Goodrich, Louisville, Ky.	63	
Goodyear, Akron, Ohio; Houston, Tex.	68	
Uniroyal, Painesville, Ohio	56	
TOTAL	240	
Adiponitriled		
DuPont, Laplace, La.	-	SRI, 1975
DuPont, Orange, Tex.	-	
DuPont, Victoria, Tex.	-	
Acrylonitrile-Butadiene-Styrene Resins^e		
Abtec, Louisville, Ky.	65	Anon., 1977j
Borg-Warner, Ottawa, Ill.	230	
Borg-Warner, Washington, W. Va.	290	
Dow, Gales Ferry, Conn.	65	
Dow, Midland, Mich.	70	
Dow, Torrance, Calif.	20	
Hammond Plastics, Worcester and Oxford, Mass.	11	
Monsanto, Addyston, Ohio	275	
Monsanto, Muscatine, Iowa	125	
Rexene, Joliet, Ill.	55	
Uniroyal, Baton Rouge, La.	200	
TOTAL	1406	

^c Capacities are flexible in plants where other elastomers such as styrene-butadiene, styrene-butadiene-vinylpyridine or PVC blends with nitrile may also be produced.

^d DuPont is the only producer making adiponitrile from butadiene. Other adiponitrile manufacturers are: Celanese Corp. (Bay City, Tex.), El Paso Natural Gas Co. (Odessa, Tex.) and Monsanto Co. (Decatur, Ala.; Pensacola, Fla.).

^e Capacity of styrene-acrylonitrile (SAN) resin included in some figures; SAN capacity considered proprietary.

Solution polymerization techniques are used to make thermoplastic SBR, a block polymer of styrene and butadiene. An outstanding characteristic is that the polymer is a rubber when cold, a plastic when hot (Allan, 1972).

Table 18 shows that the capacities of the major SBR producers exceed 3500 million pounds per year. The annual capacity of SBR latex is about 700 million pounds per year, Goodyear and Firestone being the largest producers (SRI, 1975). During 1976, 2967 million pounds of SBR rubber and latex were produced in the U.S., up 12% from 1975 figures but below peak 1973 production (3334 million lbs.) (Dept. of Comm. 1977). Figures for 1977 will probably show a surge of production as a result of the rubber strike of 1976 (Anon., 1977e).

The future of SBR (and also polybutadiene) is highly dependent on tire demand. Expected growth in the tire industry is only about 2% per year (Anon., 1977a). One factor in this modest growth is the trend to smaller cars and slower highway speeds. Also, most new cars come equipped with radial tires which give 40% better mileage than bias tires and 20% more than belted ones; therefore, tire replacement is less frequent. In 1970 only 1% of the new cars came equipped with radial tires but by 1985 this figure is expected to reach 90% (Prescott, 1976). Furthermore, when a conventional tire is replaced by a radial tire as much as 14% less SBR is used (Greene and Pennington, 1977). There has also been a decline in passenger car travel mileage. In the past, mileage has increased about 5% per year but this rate may drop to 2%. Based on tire demand and other uses, Greene and Pennington (1977) forecast that dry SBR use will grow at the rate of 2.5% per year through 1981.

b. Polybutadiene

About 720 million pounds of butadiene were consumed during 1977 in the production of polybutadiene, accounting for 18% of butadiene demand (Anon., 1977a). Approximately 85% of the total polybutadiene supply is used in auto and truck tires (Anon., 1976c), usually in blends with SBR or natural rubber. Polybutadiene enhances the resilience of SBR which reduces heat buildup in tire treads (Allan, 1972). The rest of the polybutadiene supply is used in high impact resins among other uses (Anon., 1976c).

Polybutadiene is made primarily by solution polymerization. By using different stereoregulating catalysts, polybutadienes can be made ranging from almost 100% cis to 100% trans. A solution polymerization process developed by Phillips Petroleum Co. to produce high cis content polybutadiene (>80% cis) consists of four basic steps (Figure 7):

1) butadiene and solvent purification; 2) reaction and concentration; 3) blending and solvent removal and 4) drying and packaging. The over-all conversion of butadiene to cis- polybutadiene is >98% (Anon., 1977k).

Polybutadiene is produced at 5 sites by four producers with a total annual capacity of 905 million pounds (Table 18). A total of 781 million pounds of polybutadiene elastomer, including latex, were produced domestically during 1976, an increase of about 18% over 1975 when production was depressed (Department of Commerce, 1977). Demand for polybutadiene is expected to increase 2-3% per year through 1980; however, there is a trend to substitute polybutadiene for natural rubber in tire sidewalls which would increase projected demand further (Anon., 1976c).

c. Chloroprene/Neoprene

Chloroprene (2-chloro-1,3-butadiene) is manufactured from butadiene, accounting for 7% of the total domestic butadiene demand (or about 280 million

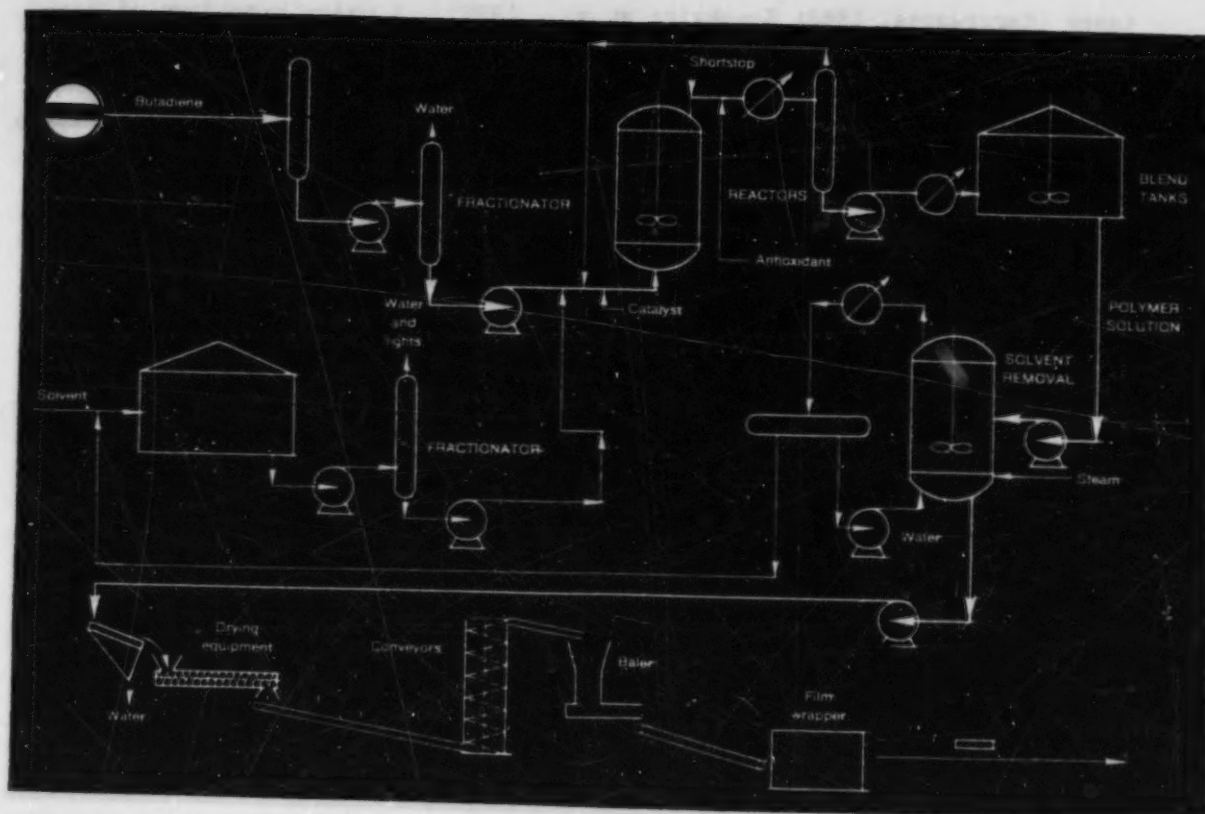
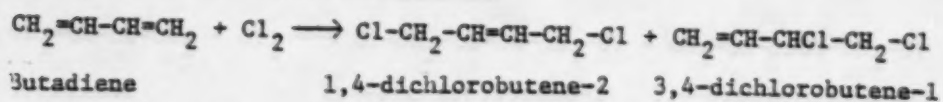


Figure 7. Production of cis-Polybutadiene (Anon., 1977k) Reprinted by Permission from Gulf Publishing Co., Houston, Texas

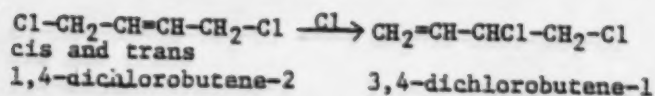
pounds/year) (Anon., 1977a). It is used in the production of polychloroprene synthetic elastomers under the trade name of Neoprene. Neoprene is used in applications requiring high gum strength or chemical, oil and weather resistance (Hargreaves, 1968; Bauchwitz et al., 1971). A major breakdown of Neoprene markets would include: exports (30%), industrial rubber goods (24.5%), automotive (19.6%), wire and cable (9.1%), construction (7%), adhesives (5.6%) and miscellaneous uses (4.2%). Future growth is forecasted to be 2.4% per year but could be slightly higher if potential applications are accepted (e.g. full-foam seats for commercial use; Anon., 1976d).

Chloroprene production utilizes butadiene as a starting material in a

i.) Chlorination of Butadiene

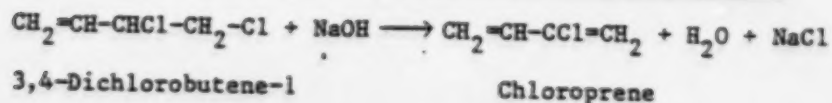


ii.) Isomerization of Dichlorobutenes



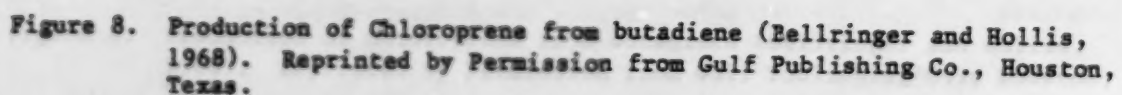
The 1,4-dichlorobutene-2 is isomerized to 3,4-dichlorobutene-1 for chloroprene but can also be used in adiponitrile manufacture (See II-B-1-e)

iii.) Dehydrochlorination of 3,4-Dichlorobutene-1



A simplified flow diagram for chloroprene production appears in Figure 8. Overall yields of 80-95% based on butadiene input have been reported (Bauchwitz et al., 1971).

There are two producers of neoprene: DuPont (La Place, La.; Louisville, Ky.) and Petro-Tex (Houston, Tex.). Their capacities total 440 million pounds/year. This capacity should be adequate for the foreseeable future (Anon., 1976d).



d. Nitrile Rubber

About 3% of the butadiene supply is used in nitrile rubber, a copolymer of acrylonitrile and butadiene. The acrylonitrile content is about 32% but may range from 18 to 50% (Saltman, 1964). The main advantage of nitrile rubber is the oil resistance imparted by the acrylonitrile component. Among uses of nitrile rubber are applications in latex (20%), hose (20%), seals and gaskets (15%), footwear (4%), adhesives and binders (8%), exports (18%) and miscellaneous mechanical goods (15%) (Anon., 1976e).

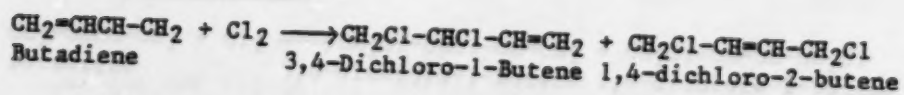
Nitrile rubber is produced by emulsion polymerization techniques similar to SBR manufacture (Section II-B-1-a). There are four major producers (Copolymer, Firestone, Goodrich and Uniroyal) with an annual capacity of 240 million pounds (Table 18). During 1976 about 170 million pounds of nitrile rubber (including latex) were produced domestically, 27 million pounds below peak 1974 production rate (Department of Commerce, 1977). Growth is predicted at 3.5% per year through 1980 (Anon., 1976e).

e. Adiponitrile/HMDA

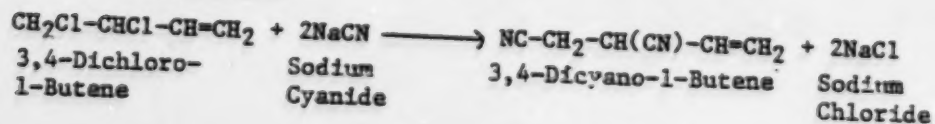
DuPont uses butadiene to make adiponitrile, which is hydrogenated to form hexamethylenediamine (HMDA), an intermediate in the manufacture of nylon 6,6. DuPont uses two processes to make adiponitrile.

The older four-step process, used since 1950, is employed at 2 of 3 DuPont plants (Victoria, Texas and La Place, Louisiana). The main steps are summarized below (Pervier et al., 1974b):

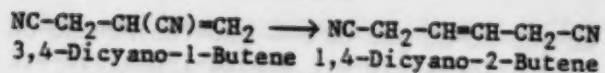
i.) Chlorination



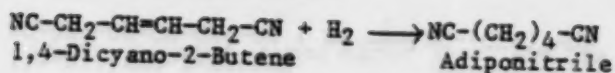
ii.) Cyanation



iii.) Isomerization



iv.) Hydrogenation



In reaction i.) above, the products can also be used in the manufacture of polychloroprene (2-chloro-1,3-butadiene) (Ericksson, 1977). Both chloroprene and adiponitrile are produced at DuPont's Victoria, Texas plant (SRI, 1975).

At the newer plant in Orange, Texas, butadiene is mixed with hydrogen cyanide in the presence of copper chromate catalysts, which forms the adiponitrile precursor, 1,4-dicyano-2-butene by direct hydrocyanation (Drinkard, 1970). The first adiponitrile plant in Europe (104 metric tons/year capacity) using this process has just been completed at Chalampe, France by Butachimie, licensed by DuPont (Anon., 1978c; Prescott, 1976). With this one exception, other companies besides DuPont do not use butadiene to produce adiponitrile, but rather use cyclohexane or acrylonitrile as a starting material (Pervier et al., 1974b).

Capacity figures for DuPont's adiponitrile plants are unavailable. About 8% of the total domestic butadiene demand (or about 320 million lbs/year) is used by DuPont in adiponitrile manufacture (Anon, 1977a).

f. Acrylonitrile-Butadiene-Styrene Resins

About 6% of the total domestic demand for butadiene (or 240 million pounds) goes into Acrylonitrile-Butadiene-Styrene (ABS) resins. ABS resins are usually produced by "graft" polymerization. A rubber is made by the polymerization of butadiene. Styrene and acrylonitrile monomers are then polymerized (grafted) directly onto the rubber.

Major markets for ABS resins include pipe (29%); automotive (18%); appliances (18%); recreational vehicles (8%); business machines and telephones

(5.2%); furniture, luggage and packaging (6.1%); exports (3.2%) and miscellaneous uses (11.5%). Among newer markets is use in recreational vehicles and smoke detectors. Growth is forecasted at 7.5% per year through 1981 (Anon., 1977j).

ABS is made by 7 producers at 11 sites for a total annual capacity (Table 18) of 1406 million pounds. Planned expansions have been announced by all producers except for Rexene Styretics, and when operational should increase total ABS capacity by at least 400 million pounds/year by 1979 (SRI, 1977; Anon., 1977l, 1977m, 1977n).

g. Miscellaneous Use

Miscellaneous uses account for about 5% (or 200 million pounds) of the domestic butadiene demand. About 76 million pounds of domestically produced butadiene were exported from the U.S. during 1976, primarily to Canada (43.6%), Mexico (37.4%) and the Korean Republic (15%) (U.S. Bureau of Census, 1976). Total exports have increased during the last 5 years (Table 19).

Included among miscellaneous uses of butadiene are several derivatives. For example, butadiene is used in the preparation of the fungicide Captan and the insecticide Phygon. It is also used to prepare Sulfolane, a product used as a process solvent. These reactions were discussed in Section I-D-1. As discussed (Section II-A-1-b) small amounts of butadiene are used in the manufacture of cyclooctadiene, and cyclododecatriene.

Another use of butadiene is in methyl methacrylate-butadiene-styrene (MBS) terpolymers used as impact modifiers in rigid poly(vinyl chloride) compounds. MBS has major applications in packaging and in building and construction. A typical MBS formulation contains 75 parts butadiene to 25 parts styrene as a substrate; the final polymer contains 60 parts substrate, 20 parts styrene, and 20 parts methyl methacrylate (Purcell, 1976).

Table 19
Exports of U.S. Butadiene Monomer^a

	1976	1975	1974	1973	1972
Total Quantity (lbs.)	76,106,477	73,019,505	70,180,555	64,201,585	28,428,748
Where Exported (%)					
Argentina	0.4	0.5	<0.1	-	0.2
Australia	-	1.8	-	-	-
Brazil	0.9	4.7	-	18.8	-
Canada	43.6	29.9	32.9	19.4	0.8
Japan	0.6	-	-	-	-
Korean Republic	15.0	-	-	-	-
Mexico	37.4	46.7	67.0	61.7	99.0
Netherlands	-	16.3	-	-	-
Others	-	0.1	<0.1	0.1	0.2

^a Commodity number 5120996

Source: U.S. Bureau of Census. (1972-1976)

Butadiene is also used in the production of polybutadiene by the Arco Chemical Co. This is a liquid resin containing 85-100% butadiene, either as a homopolymer or as a copolymer with styrene or acrylonitrile. Polybutadiene is also referred to as an hydroxyl terminated polybutadiene. Carboxyl terminated polybutadienes are called Hycar, a trademark of B.F. Goodrich (Buchhoff, 1975).

Small amounts of butadiene were used in the manufacture of nitrile barrier resins. The use of these resins, which contained acrylonitrile (a suspected carcinogen), has been banned by the FDA for beverage containers (Kennedy, 1977). Two barrier resins which contained butadiene were (Nemphos et al., 1976):

Barex (Sohio), a 90% copolymer of 74% acrylonitrile and 26% methylacrylate + 10% butadiene rubber graft

Cycopac (Borg-Warner), a 90% copolymer of 74% acrylonitrile and 26% styrene + 10% butadiene rubber graft.

h. Projected Uses

BASF (Ludwigshafen, W. Germany) and DuPont are studying the feasibility of producing adipic acid from butadiene. BASF has reported a 49% yield of adipic acid using a rhenium-chloride-catalyzed carbonylation of butadiene (Prescott, 1976).

Snam Progetti (Milan, Italy) has developed an ethylene-butadiene copolymer (EDM) (Bruzzzone, 1973). Advantages of EDM are good thermal and solvent stability.

Brownstein (1976) speculated that butadiene could be used commercially to make styrene in a Diels-Alder reaction. This would be possible if benzene, the principal raw material for styrene, increased in price to exceed the price of butadiene. Currently, however, butadiene is not cheap enough to be considered a serious alternative starting material for styrene production.

A new butadiene polymer, syndiotactic 1,2-polybutadiene, has been developed by the Japan Synthetic Rubber Co. with potential applications in thermoplastics, thermosetting, resin, coating, rubber and adhesives. (Takeuchi et al., 1974a and 1974b). Specific uses could include plastic stretch film, cellular sponge shoe soles, and as a matrix in a letterpress plate system.

i. Alternatives to Use

According to Ericksson (1977) natural rubber could replace a synthetic elastomer in some uses. He suggests that a synthetic elastomer is preferred in 60% of all end-uses while natural rubber is preferred in 20% of uses. The balance of uses can swing between the two depending on price. Price has been an important factor, for example, in the use of SBR. SBR has few major technical advantages over natural rubber and is inferior to it in several respects. Its prevalence, according to Allan (1972) is due to economic factors: its stable price and particularly that it can be bought as an oil-extended material.

2. Oligomers

As discussed in the section on chemical reactions (I-D), vinylcyclohexene can be used in some preparations for insecticides and plasticizers and as an intermediate in preparing aliphatic hydrocarbons and antioxidants.

Cyclododecatriene is the starting material for nylon 12 production; cyclododecatriene is converted to dodecanolam, the precursor of nylon 12. Cyclododecatriene is also used in nylon 6/12 and Qiana nylon fiber production. It is first converted to dodecanedioic acid. DuPont produces both Qiana and nylon 6/12 (Anon., 1972). Another use of cyclododecatriene is in the production of hexabromocyclododecane, a chemical used in flame retardants for expanded polystyrene. In the U.S., hexabromocyclododecane is manufactured by the Michigan Chemical Corporation (St. Louis, Mich.) (S.R.I., 1975).

The major use of cyclooctadiene is as a third monomer in ethylene-propylene terpolymer such as DuPont's Nordel^R. DuPont's capacity for Nordel is 120 million pounds at Beaumont, Texas (SRI, 1975). Other uses or potential applications of cyclooctadiene cyclododecatriene are listed in Tables 20 and 21.

C. Entry into the Environment

Limited monitoring data indicate that butadiene monomer can enter the environment during several aspects of production and use. In addition, butadiene has been identified as a component of urban air. Butadiene and oligomers have been identified in the workroom of synthetic rubber facilities. Monitoring studies are discussed in sections which follow.

1. From Production

Figure 9 shows emission points for gaseous, solid and liquid wastes generated during butadiene manufacture. In addition fugitive emissions can occur at valves, seals, vents and leaks in equipment. Unfortunately, the chemical constituents of these wastes have not been quantified. In the absence of monitoring data, it is difficult to assess the likelihood of environmental contamination by butadiene or oligomers during manufacture.

2. From End Product Manufacture

a. Workroom Levels

Occupational exposure levels to butadiene and oligomers have not been extensively reported in the U.S. and Western European literature. In the U.S., workroom exposure to butadiene is limited by the Occupational Safety and Health Administration (OSHA) to an 8-hour time-weighted average of 1,000 ppm (2,200 mg/m³) (29 CFR 1910.1000). No OSHA standards exist for butadiene oligomers.

Table 20
Derivatives of Cyclooctadiene and
Possible Uses (Ono and Kihara, 1967)

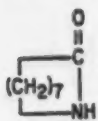
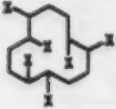
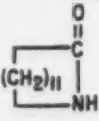
<u>Name</u>	<u>Derivative</u>	<u>Structure</u>	<u>Possible Uses</u>
Octyl Lactam			Nylon 8
Epoxy-cyclooctene			Paints, Adhesives
Tetrahalo-cyclooctane			Fire- retardant
Suberic Acid	$\text{HOOC}(\text{CH}_2)_6\text{COOH}$		Polyesters, Polyamides, Plasticizers
Octamethylene Diamine	$\text{NH}_2(\text{CH}_2)_8\text{NH}_2$		Polyamides, Diisocyanate
Octamethylene Diisocyanate	$\text{OCN}-(\text{CH}_2)_8\text{NCO}$		Polyurethanes
4-Octenedioic Acid	$\text{HOOC}(\text{CH}_2)_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{COOH}$		Unsaturated Polyesters, Alkydes
Ter-monomer	—		For EPT Rubber

Table 21
Derivatives of Cyclododecatriene
and Possible Uses (Ono and Kihara, 1967)

<u>Name</u>	<u>Structure</u>	<u>Possible Uses</u>
Hexahalo, Cyclododecane		Fire-retardant
Epoxy-cyclo dodecadiene		Paints, Adhesives
Lauryl lactam		Nylon 12
Dodecanedioic acid	$\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$	Polyesters, Polyamides, Plasticizers
Dodecamethylene diamine	$\text{NH}_2(\text{CH}_2)_{12}\text{NH}_2$	Polyamides, Diisocyanate
Dodecamethylene diisocyanate	$\text{OCN}-(\text{CH}_2)_{12}-\text{NCO}$	Polyurethanes
4,8-Dodecadienedioic acid	$\text{HOOC}(\text{CH}_2\text{CH}_2\text{CH}=\text{CH})_2\text{CH}_2\text{CH}_2\text{COOH}$	Unsaturated Polyesters; alkydes

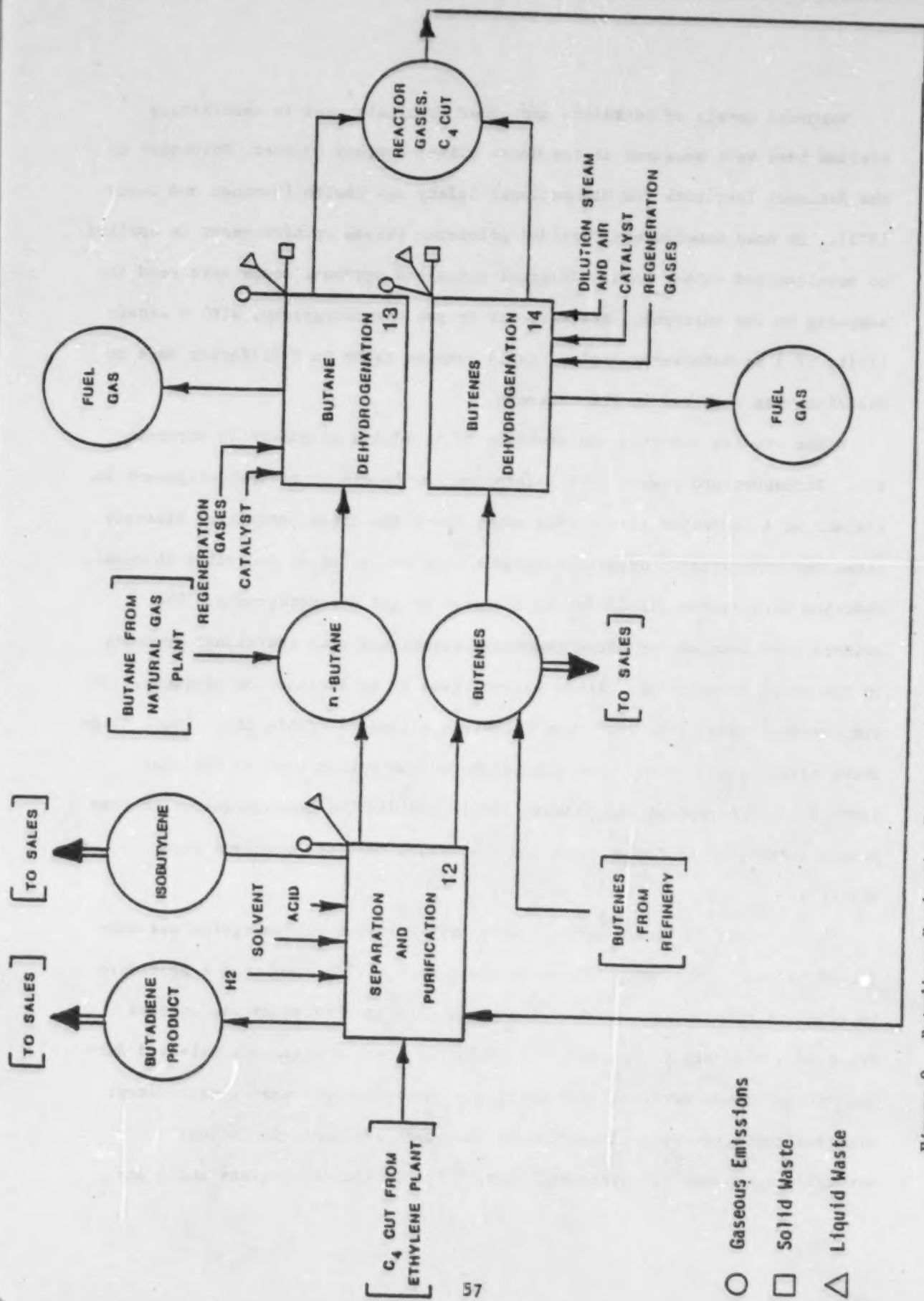


Figure 9. Butadiene Production Processes Identifying Waste Emissions (Parsons et al., 1977)

Workroom levels of butadiene and other chemicals used to manufacture braided hose were measured at the Gates Rubber Company (Denver, Colorado) by the National Institute for Occupational Safety and Health (Gunther and Lucas, 1973). In hose manufacture, braided polyester thread reinforcement is applied to unvulcanized rubber hose. Charcoal tubes and personal pumps were used for sampling in the workroom. Analysis was by gas chromatography, with a sensitivity of 5 mg butadiene/sample. In 14 samples taken on 2 different days no butadiene was detected in the workroom.

Other studies reported the presence of butadiene oligomers in workroom air. Rappaport and Fraser (1977) detected low levels of several oligomers in the air of a passenger tire curing room, where the tread portion of bias-ply tires was vulcanized. Organic compounds were collected on activated charcoal, desorbed with carbon disulfide and analyzed by gas chromatography. The authors only sampled for those compounds associated with individual products in the stock formulation, either as additives or as degradation products. Of six compounds detected, four were butadiene oligomers (Table 22). These oligomers probably originated from cis-polybutadiene rubber used in the tire formulation. Rappaport and Fraser (1977) consider the concentrations of compounds identified in Table 22 so low that acute toxicity problems seem unlikely.

The presence of butadiene oligomers during rubber vulcanization was confirmed in the laboratory. Rappaport and Fraser (1977) developed a procedure to simulate tire vulcanization. The stock used in this study was uncured tread of a bias-ply passenger tire. Volatile organic compounds released during vulcanization were analyzed using gas chromatography-mass spectrometry; eighteen compounds were identified in the stock effluent, including 4-vinylcyclohexene, 1,5-cyclooctadiene, 1,5,9-cyclododecatrienes and 3 un-

Table 22
Air Concentrations of Butadiene Oligomers
and Other Compounds in a Passenger Tire Curing Room
(Rappaport and Fraser, 1977)

Compound ^a	Location ^b	Concentration	
		Mean ^c (ppb)	Relative Std. Dev. (%)
4-Vinylcyclohexene	1	71.0	11.9
	2	92.3	21.6
1,5-Cyclooctadiene	1	6.27	23.0
	2	6.45	18.1
1,5,9-Cyclododecatrienes ^d	1	7.21	21.1
	2	15.8	29.7
Toluene	1	1120	26.9
	2	1160	17.4
Ethylbenzene	1	78.2	29.0
	2	112	25.7
Styrene	1	84.6	25.4
	2	111	18.2

^a Only these compounds were quantified; however, these are not the only components released during vulcanization.

^b Location 1 directly in center of passenger tire curing area; location 2 at periphery of passenger tire curing area.

^c Mean of 9 samples/compound.

^d Cis and trans isomers.

identified butadiene trimers. The probable source of these oligomers is the cis-polybutadiene rubber used in the stock formulation.

In contrast to U.S. and Western European literature, several Russian papers identified the levels of butadiene in workroom air (Table 23). Concentrations ranged from 15-40 mg/m³ in rubber vulcanization areas, 0.3-400 mg/m³ in areas of synthetic rubber production, and 0.7-1.7 mg/m³ at a dimethyl terephthalate production facility (Table 23). The oligomer, 4-vinylcyclohexene, was measured at average levels of 1,200-2,400 mg/m³ (and a maximum of 3,000 mg/m³) at its site of manufacture (Bykov, 1968 in IARC, 1976a).

b. Air Emissions

Butadiene has been identified as a minor constituent of atmospheric emissions resulting from SBR production using emulsion polymerization techniques (Table 24). Based on information from 3 SBR manufacturers detailing all emission constituents, Pervier et al. (1974a) identified 2 sources of butadiene emissions: i) butadiene absorber vents and ii) fugitive emissions. The first source results after polymerization, when unreacted butadiene is flashed off, compressed, condensed, and recycled. The non-condensable contaminants (mostly air) are vented to the atmosphere through an absorption column. Small amounts of butadiene, about 0.0001 pounds of butadiene per pound of SBR produced, are vented along with the non-condensibles.

Fugitive emissions total about .00085 pounds of butadiene per pound of SBR produced and are attributed to these sources:

1b butadiene/lb SBR

reactor section	.00034
monomer recovery	.00034
tank farm	.00017

Table 23
Levels of Butadiene in the
Workplace at Production Facilities
in the U.S.S.R.

Operation	Butadiene Concentration (mg/m ³)	Reference
Rubber Vulcanization	15-20 32-40	Volkova et al., 1970 Volkova et al., 1969
Synthetic Rubber Production	0.3-0.5	Bashirov, 1971
SBR Production	85-236.4 20-400	Lukoshkina et al., 1973 Konstantinovskaja, 1970
	exceeded MAC ^a by 1.5-3.0 times	Babanov, 1960
Dimethyl Terephthalate Production	0.7-1.7	Lyashenko and Sidenko, 1974

^a Mean acceptable concentration.

Tank farm emissions result from butadiene storage tanks (30,000-600,000 gallon capacity), although many plants receive butadiene by pipeline and have no facilities to store it (Pervier et al., 1974a).

The total amount of butadiene emitted is only a small fraction of total emissions (Table 24). Pervier et al. (1974a) described the SBR industry as a "low (air) polluter" and recommended that no in-depth study of SBR emulsion polymerization be undertaken.

Ripp (1967) listed several possible sources of environmental contamination during butadiene manufacture and synthetic rubber end-use in the U.S.S.R.: polymerization areas; charge preparation and monomer distillation areas; extraction of butadiene by chemoabsorption from a copper-ammonia complex; and the butadiene storage areas.

Pervier et al. (1974b) evaluated atmospheric emissions from the older three-step process employed to manufacture adiponitrile from butadiene and described emissions as "moderate." Various phases of production were sampled for hydrocarbons, particulates, CO, NO_x and SO_x. Nitrogen oxides comprised the major portion of detectable air pollutants. For hydrocarbons, a total of 0.0254 pounds were emitted per pound of adiponitrile produced. Butadiene comprised only 3.8% of this total. Small amounts of butadiene were detected in two streams associated with chlorination.

Ripp (1967) sampled the air near a plant in the U.S.S.R. where butadiene was produced by butane dehydrogenation and then used on-site in rubber production. Samples were taken during July and August (170 samples; air temp. 25-30° (units of temperature are unspecified)) and during November and December (150 samples; air temp. -7 to -15°). Three sample sites exceeded 3 mg/m³ ("the proposed maximum single acceptable value") during July and August: 50 and 70 meters from the butadiene extraction shop (6.12 and 6

mg/m³, respectively) and 30 meters from the monomer distillation shop.

These same sites contained less butadiene during the winter: 3.2-3.5 mg/m³ at 20 meters; 0.2-0.7 mg/m³ at 500 meters; not detected at 1500-2000 meters. Ripp (1967) recommended that particular attention be directed toward "sealing all systems" in the shops, especially during the summer.

c. Water Effluent

Day (1975) identified liquid emission points from synthetic rubber manufacturing processes. For crumb rubber production, the following processes result in wastewater generation: monomer recovery; rubber coagulation; crumb dewatering; equipment cleanout; and area washdown. Monomer recovery wastewater contains butadiene, but the levels were not given; chemical constituents of the other streams were not given. In latex rubber manufacture, the principal liquid effluents are generated by monomer removal, equipment cleanout, and area washdown. In monomer removal, excess monomer is steam or vacuum stripped prior to latex shipment; this wastewater contains butadiene at unspecified levels. As for crumb rubber production, the composition of waste streams from latex rubber is not detailed.

Butadiene was not identified as a constituent of wastewater effluents from synthetic rubber manufacture in a survey of that industry designed to develop effluent limitation guidelines. Since butadiene is recovered and returned to the monomer supply plant, it has no impact on the wastewater, according to an EPA report (EPA, 1974a). Butadiene and other organic compounds were reported by Bordo (1951) to be constituents of wastewaters from the Huls Chemical Works in Germany. An experimental treatment procedure, involving steam treatment and filtering, resulted in complete removal of butadiene.

3. From Product Use

The Russian investigators, Sopach and Krotova (1973), studied the migration of butadiene monomer and other components of butadiene rubber component constituents into aqueous solutions. Polybutadiene rubber suspensions (0.3-3 g) were mixed with 10 ml of distilled water and allowed to stand for 18 hours. The test used to detect butadiene in the solution has been described (Section II-F; based on interaction of butadiene and p-NO₂-benzenediazolium in acetic acid). Butadiene compounds were detected in aqueous solutions at 2-3.3 mg/l when the rubber content of the water was 30%.

No data are available on the release of butadiene under actual or simulated use conditions.

4. From Storage and Transport

Butadiene is often stored in tank farms, which are diked to retain spills and leakages and to control fire spreads (EPA, 1974a). Pervier et al. (1974a) reported emissions from tank farms of .00017 pound butadiene per pound of SBR produced at a synthetic rubber facility.

Transportation accidents of butadiene would pose a dangerous fire hazard since butadiene is a gas at ambient temperatures; the flammable limits in air are 2.0 to 11.5%. The vapors are heavier than air and may travel a considerable distance to a source of ignition and flash back; therefore butadiene is shipped as a liquid in pressure-type containers. A spill of liquid will, however, float and boil on water, producing a flammable visible vapor cloud (CHRIS, 1974). In Section V the formation and hazards of vapor cloud formation are reviewed.

5. From Other Sources

Butadiene has been identified as a constituent of gasoline, ambient urban air and cigarette smoke.

a. Gasoline

Since butadiene is made from petroleum feedstocks it is not surprising that it is found in gasoline. Stevens and Burleson (1967) measured <0.002 ppm butadiene in liquid gasoline and 0.001 ppm in gasoline vapor which represented an extremely small fraction of the total compounds detected (total of all 27 compounds found was 33.15 ppm and 17.04 ppm in liquid and vaporized gasoline, respectively). Neligan (1962) measured 0.02-0.06 ppm butadiene in diluted automobile exhaust. When samples were irradiated for 4 hours under ultraviolet light, levels of butadiene ranged from undetectable to 0.01 ppm, suggesting photochemical breakdown in air (discussed in more detail in Section II-E-1-b). Under both irradiated and nonirradiated conditions, butadiene was only a small constituent of all hydrocarbons identified (Table 25).

b. Urban Air

Low levels of butadiene (<10 ppb or 0.02 mg/m^3 ; Table 26) have been measured in urban ambient air. Data have been reported as ppb or ppm, but have also been converted to mg/m^3 in Table 26. Neligan (1962) suggests that a major source of low-boiling hydrocarbons (i.e., butadiene) could be gasoline from automobile exhaust. Altshuller et al. (1971) suggested other sources: gasoline evaporation, natural gas losses, and diffusion through soil from petroleum deposits.

In this study Altshuller et al. (1971) also measured the hydrocarbon composition of the atmosphere in downtown Los Angeles and Azusa, California, taking hourly and daily measurements over several weeks. The concentration of butadiene averaged 2 and 1 ppb in Los Angeles and Azusa, respectively (see Table 26). Values for 13 other aliphatic hydrocarbons were also reported; butadiene comprised only 0.04-0.05% of all aliphatic hydrocarbons in both localities.

Table 25
Analyses of Automobile Exhaust for 44 Hydrocarbons,
Including 1,3-Butadiene (Neligan, 1962)

<u>Sample^a</u>	<u>1,3 Butadiene</u> (ppm volume)	<u>All Hydrocarbons</u> (ppm volume)
Diluted, Nonirradiated		
1	0.02	1.62
2	0.04	2.14
3	0.06	4.57
Diluted, Irradiated		
1A	0.005	1.46
2A	-	1.65
3A	0.01	3.11
4A	0.01	2.51

^aSamples analyzed by gas chromatography; "Representative" automobile exhaust was obtained from a vehicle operating under normal traffic conditions. The composition of diluted exhaust was determined for 4 samples by gas chromatography. Each sample was then irradiated for 4 hours under ultraviolet light.

Table 26
Ambient Air Levels of 1,3-Butadiene

Locality	Method of Determination	Level		Reference
		ppb	mg/m ³	
Downtown Los Angeles, Calif.	averaged daily, measured over 14 days	2	0.00442	Altshuller et al., 1971
Azusa, Calif.	averaged daily, measured over 12 days	1	0.00221	Altshuller et al., 1971
Riverside, Calif.	data from 6 afternoons during air pollution episode	<0.1-0.7	<0.000221-0.001547	Stephens and Burleson, 1967
Riverside, Calif.	data from 3 early mornings	2.6-9.0	0.00575-0.01989	Stephens and Burleson, 1967
Los Angeles, Calif.	data from 16 samples on 9 days	not detected to 9.0 (see Table 27)	not detected to 0.01989	Neligan, 1962

Diurnal data for Los Angeles revealed that the midafternoon concentration of faster reacting hydrocarbons, including 1,3-butadiene, 1-butene, isobutene, xylenes, and 1,2,4-trimethylbenzene decrease by a factor of three from morning peak hours. These hydrocarbons together constitute only a few percent of the total hydrocarbon composition.

Slightly higher butadiene levels were reported by Stephens and Burleson (1967) for Riverside, California. On three mornings, butadiene levels were 2.6, 2.4 and 9.0 ppb. Levels measured during 6 afternoon ranged from <0.1-0.7 ppb. In Los Angeles, Neligan (1962) measured up to 9 ppb of butadiene (Table 27).

c. Cigarette Smoke

Osborne et al. (1956) measured 19 components of cigarette smoke. In cigarettes made from four kinds of tobacco (Bright, Burley, Cased Burley and a blend of Bright and Burley) butadiene made up $0.95 \text{ g} \times 10^{-2}$ mole % of the total volume of all gas phase components.

d. Fire

Insignificant amounts of butadiene might enter the environment during fires. For example, the combustion of a piece of rubber foam 7.6 cm square resulted in the evolution of 4 ppm (8.84 mg/m^3) butadiene, in a smoke chamber $0.6 \times 0.9 \times 0.9$ meters (Adams, 1977).

The experimental pyrolysis ($325\text{--}400^\circ\text{C}$) of polybutadiene in a vacuum yielded about 1.5 wt% 1,3-butadiene of the total volatile components (Madorsky, 1964). No butadiene oligomers were specifically identified as volatile components but Madorsky (1964) assumed dimer formation. The actual yield of butadiene may have been higher; dimerization on standing may have contributed to the low yields.

Table 27
Ambient Air Analyses for 44 Hydrocarbons, Including
1,3-Butadiene, from the Central Los Angeles
Business District (Neligan, 1962)

<u>Date</u>	<u>Sample No.^a</u>	<u>1,3-Butadiene</u>		<u>All Hydrocarbons</u>
		<u>ppm volume</u>	<u>mg/m³</u>	
8/12/60	A1	- ^b	-	0.348
	A2	-	-	0.469
9/14/60	A3	0.004	0.00884	0.228
	A4	0.002	0.00442	0.271
9/27/60	A5	-	-	0.956
	A6	<0.0005	0.001105	0.921
9/28/60	A7	0.004	0.00884	0.702
	A8	0.005	0.01105	1.238
10/4/60	A10	0.001	0.00221	0.288
10/26/60	A11	0.003	0.00663	0.666
	A12	0.003	0.00663	0.546
11/1/60	A13	0.005	0.01105	1.117
	A14	0.006	0.01326	1.624
11/2/60	A15	0.004	0.00884	0.621
	A16	0.004	0.00884	0.622
11/18/60	A17	0.009	0.01989	1.341

^asamples analyzed by gas chromatography

^bdash (-) indicates level below detection limits

D. Waste Handling

Butadiene itself is not a major component of wastewaters. The handling of wastes from butadiene manufacture is discussed in this section. Waste waters are generated during several phases of butadiene manufacture. For production via dehydrogenation of n-butane, waste streams are produced from: i.) scrubbing the gases used to periodically burn coke from the catalyst surface, ii.) from the steam ejector-barometric condenser systems used to produce vacuum in the reactors, and iii.) from the final recovery of butadiene product (EPA, 1974b).

Major contaminants include residue gas, tars, oils, and unspecified soluble hydrocarbons (Gloyne and Ford, 1970). When butadiene is produced as a co-product of ethylene manufacture, wastewaters are generated from the final recovery unit (EPA, 1974b). The composition of wastewater from several butadiene plants is presented in Table 28 for total flow, chemical oxygen demand, biological oxygen demand and total organic carbon. The variation in flow is due to the use of steam ejectors to produce reactor vacuum (in Table 28 plants 1 and 2, using the Houdry Process, operate at low pressures) (Parsons et al., 1977).

Several patents describe the treatment of butadiene wastewaters. However, actual processes used by the industry have not been described in available literature. During 1977, a multimillion dollar secondary wastewater treatment system went into operation at Firestone's Orange, Texas Petrochemical Center (Firestone, 1977).

In a patent assigned to the Petro-Tex Chemical Corporation, Woerner (1967) described a method for the simultaneous separation of butadiene from carbonyl compounds (which are contaminants) and the disposal of boiler blowdown water (liquid formed during cleaning or purging of boilers and is characterized by

Table 28
Characterization of Waste Streams from Butadiene
Manufacture (EPA, 1974^b)

Plant No.	Process	Flow gal/1,000 lb (mg/l)	COD ^a lb/1,000 lb (mg/l)	BOD5 ^b lb/1,000 lb (mg/l)	TOC ^c lb/1,000 lb (mg/l)
1.	Dehydrogenation, Extractive Distillation	1,160	3.23 (334)	2.96 (306)	
2.	Dehydrogenation, Extractive Distillation	1,451	245 (20,200)	72 (5,960)	
3.	Co-product of ethylene Extractive Distillation	88	1.120 (1,525)	0.547 (745)	0.554 (755)
4.	Co-product Ethylene Extractive Distillation	339	3.899 (1,378)	1.183 (418)	1.545 (546)
5.	Co-product of Ethylene Extractive Distillation	183	1.042 (683)	0.165 (102)	0.313 (205)

^aCOD = chemical oxygen demand

^bBOD5 = biological oxygen demand at 5 days

^cTOC = total organic carbon

high heat, pH and concentration of solids). Woerner's process involves using such wastewater as a treating composition to remove oxygenated compounds from organic compounds such as butadiene. Otherwise, this liquid must be treated prior to discharge.

Cunningham (1971), in a patent assigned to Phillips Petroleum, outlined a process for handling oxygenated by-products (e.g., carboxylic acids, aldehydes, ketone) of butadiene manufacture using the oxidative dehydrogenation process. Under normal operating conditions, such by-products would be vented to the atmosphere and/or discharged with wastewater. The invention involves condensing oxygenated hydrocarbons with steam and recycling the condensate for catalyst regeneration.

Hinton and Cottle (1972) developed a process for Phillips Petroleum to purify effluent containing oxygenated hydrocarbons resulting from oxidative dehydrogenation processes. The procedure involves steam stripping and neutralization, and water freed of oxygenated hydrocarbons is converted into steam for use as a steam stripping medium.

Hutson and Riter (1972; patent assigned to Phillips Petroleum) developed a process to biologically treat purge water containing oxygenated hydrocarbons. This water is treated with aerobic microorganisms, then stripped with a hot gas to reduce the concentration of oxygenated hydrocarbons.

Pruessner and Mancini (1966) suggested treating by-products from petrochemical manufacture, including butadiene, by employing an extended aeration activated sludge system; they reported about 99% removal of BOD after 3 days. Activated sludge treatment systems are used to treat wastewater resulting from several processes involving butadiene (summarized in Gloyna and Ford, 1970).

The Environmental Protection Agency listed several treatment systems available to manufacturers of butadiene via dehydrogenation ("best available technology economically achievable", see Section V) (Train, 1976). One system includes steam stripping of the process wastewaters in a closed system to reduce the organic content of the raw waste load (COD can be reduced by 65-85%), followed by standard biological treatment (e.g., extended aeration or activated sludge). Biological treatment can reduce residual COD by 75% and BOD by 99%. Another method is the application of activated carbon systems to biologically treated effluents. The EPA suggested that a combination of the above technologies is possible. An economic impact assessment was carried out for four combinations (or levels) of treatment alternatives (Singer, 1976). These alternatives are listed below:

Level I

1. Steam stripping of the most concentrated wastewater stream.
2. Combining the stripper bottoms with the remaining wastewater for activated sludge bio-treatment.
3. Activated carbon adsorption of the bio-system clarified effluent.

Level II

1. Steam stripping the entire butadiene plant wastewater.
2. Activated sludge bio-treatment of the stripper bottoms.
3. Activated carbon adsorption of the bio-system clarified effluent.

Level III

1. Steam stripping of the most concentrated wastewater stream.
2. Combining the stripper bottoms with the remaining wastewater for activated sludge bio-treatment.

Level IV

1. Steam stripping the entire butadiene wastewater.
2. Activated sludge bio-treatment of the stripper bottoms.

Level II was found to be the more expensive technology according to the economic report of Singer, 1976.

E. Fate and Persistence in the Environment

1. Degradation in the Environment

The biological and chemical degradation patterns of butadiene are reviewed in this section.

a. Biological Degradation

One paper was available which suggests the possibility of biological breakdown. Watkinson and Somerville (1975) isolated a *Nocardia* species (sp. 249) from soil samples capable of using butadiene as a sole carbon and energy source; butadiene oxidation is an inducible system in this organism. To elucidate the breakdown pathway, the following parameters were measured: respiration, isocitrate lyase concentrations, lipid fatty acid composition patterns, and growth. The authors conclude that in this *Nocardia* species metabolism proceeds via formation of butadiene monoepoxide, a β,γ -unsaturated α -ketoacid, acrylate, lactate and finally, pyruvate.

b. Chemical Degradation

1) Atmospheric Reactions

Photochemical Reactions. Butadiene participates in atmospheric photolysis reactions. Stevens and Burleson (1967) collected ambient air samples, (Riverside, Calif.), in the morning before much photolysis had taken place. Three samples initially contained 9.0, 2.6, and 2.4 ppb butadiene. These were subjected to ultraviolet light (blacklite bulbs), and after 1 hour, the amount of butadiene was less than half of the original sample and was not detectable after 4 hours; 2 samples were measured every hour (Table 29). Two other samples which had been kept in the dark had relatively unchanging butadiene concentrations even after 24 hours (Table 29).

Table 29
Samples of Ambient Air Analyzed for Butadiene (and ~25 Other
Light Hydrocarbons) in Riverside, California and then Exposed
to Ultraviolet Irradiation (A) or Darkness (B)
(Stephens and Burleson, 1967)

A. Ambient Air Samples Exposed to Ultraviolet Irradiation^a

Hours Sample Irrad. with U.V.	Butadiene Concentration ^a (ppb) ^b		
	12/22/65	3/3/66	3/10/66
0 (initial)	9.0	2.4	2.6
1	2.0	1.0	-
2	0.6	0.6	-
4	0.1	0.0	-
8	0.0	0.0	-
17	0.0	-	-
20	-	0.0	-
24	0.0	0.0	0.0

B. Ambient Air Samples Kept in Darkness^a

Hours Sample Kept in Dark	Butadiene Concentration ^c (ppb) ^b	
	3/3/66	3/10/66
0 (initial)	2.0	2.8
0.75	2.0	-
24	2.0	2.6

^aAll samples taken at the Riverside County Building of Health and Finance between 07:00-08:25 PST. Weather conditions were as follows: 12/22/65 partly cloudy, calm, 45-50°F, light haze; 3/3/66 sky clear, wind 5-7 mph N.W., 40-45°F, moderately heavy haze; 3/10/66 sky clear, wind 0-1 mph, 55-60°F, heavy haze

^b1 ppb = 0.00221 mg/m³

^cConcentrations of other light hydrocarbons ranged from 1.3-310.5 ppb on 12/22/65 (x = 41.3, S.D. = 65.0), 1.0-62.4 ppb on 3/3/66 (x = 12.3, S.D. = 16.2), and 1.2-70.5 ppb on 3/10/66 (x = 16.6, S.D. = 21.0)

Reaction with Oxides of Nitrogen and Ozone. The formation of photochemical smog is triggered by the atmospheric photooxidation of hydrocarbons in the presence of oxides of nitrogen. Irradiation of air containing hydrocarbons and oxides of nitrogen leads to the oxidation of NO to NO₂, the oxidation of hydrocarbons and the formation of ozone. Several investigators have compared the reactivity of hydrocarbons with nitrogen oxides under laboratory conditions and found that rates for individual hydrocarbons vary widely. Butadiene is one of many hydrocarbons for which data are available.

Huess and Glasson (1968) mixed air containing 2 ppm butadiene and 1 ppm nitric oxide, and irradiated the mixture in a smog chamber for 6 hours. At the end of this period, 92% of the butadiene had reacted (Table 30). The rate of NO₂ formation in the presence of butadiene and nitric oxide was calculated as 25.0 ppb/minute in two determinations. For comparison, this rate varied from 1.6 to 170 ppb/minute in 25 hydrocarbons tested ($\bar{x} = 19.2 \pm 33.6$ (SD)). The following classes of hydrocarbons are given in order of increasing rates of NO₂ formation: benzene, paraffins, monoalkylbenzenes, terminal olefins, multialkylbenzenes, 1,3-butadiene, and olefins with internal double bonds.

Glasson and Tuesday (1970a) determined the reactivity of 81 hydrocarbons, including butadiene, in the atmospheric photooxidation of nitric oxide. Analyses were made with a long-path infrared spectrophotometer. For butadiene, the nitric oxide photooxidation rate averaged 4.3 ppb/minute in two determinations (Table 30). This rate for 41 olefins tested ranged from 1.5 to 59 ppb/minute ($\bar{x} = 9.5 \pm 12.9$ (S.D.)).

The products formed in the photooxidation of butadiene and nitrogen oxide include the following: acrolein, aliphatic aldehydes, ethylene, formaldehyde,

Table 30
Photooxidation of 1,3-Butadiene and Nitric Oxide

	Altshuller et al. (1966) ^a	Huess and Glasson (1968) ^b	Glasson and Tuesday (1970a) ^c
Reactants (ppm)			
Butadiene	3.3	2	1
Nitric oxide	0.85 ^d	1	0.4
% Butadiene reacted	83%	92%	NR
Rate NO ₂ formation ^e	NR	25.0 ppb/min	4.3 ppb/min
O ₃ rate	NR	4.05 ppb/min	NR
Product Yields (ppm):			
Acrolein	1.0	0.73	
Aliphatic aldehydes	1.15	NR	
Ethylene	0.022	NR	
Formaldehyde	0.85	0.80	
Ozone	NR	0.48	
Peroxyacetyl nitrate	NR	0.02	

NR = not reported

^areactants irradiated in a large chamber; average residence time 180 min.

^breactants irradiated in a smog chamber for 6 hours at 95°F

^creactants irradiated in long path cell at 79°F

^dnitric oxide plus nitrogen dioxide formed by thermal oxidation (5-10% of total)

^eaverage rate to the half-time

ozone and peroxyacetyl nitrate (Altshuller et al., 1966; Huess and Glasson, 1968). The yields of these products are given in Table 30.

The data just discussed above are for the photooxidation of nitric oxide. Glasson and Tuesday (1970b) investigated whether thermal oxidation of nitric oxide might be important as well. In particular, the authors wanted to determine if this reaction might be partially responsible for the night time conversion of nitric oxide to nitrogen dioxide in polluted atmospheres. They determined that for dienes, the photooxidation of nitric oxide is faster than the corresponding thermal oxidation. As a measure of reaction time, $t_{1/4}$ was calculated, defined as the time necessary to convert 25% of the initial concentration of nitric oxide to nitrogen dioxide. For butadiene, the $t_{1/4}$ for thermal oxidation was 311 minutes while for photooxidation $t_{1/4}$ equaled 20 minutes (both reactions were carried out at 5 ppm butadiene and 2 ppm NO). The authors concluded that for butadiene and 5 other dienes investigated, diene-promoted thermal oxidation will be relatively unimportant in polluted atmospheres compared to photooxidation.

Ozone forms in the atmosphere when the NO_2 levels are about 25 times that of NO. When ozone concentrations are 0.25 ppm or greater, ozone and olefins react at appreciable rates (Seinfeld, 1975). Hanst et al. (1959) determined rate constants for the reaction of ozone with 13 different olefins. For butadiene, $k = 0.012 \text{ ppm min}^{-1}$; for all olefins tested k ranged from 0.0001 to 0.24. The rate of reaction between ozone and olefin was second order, being proportional to the product of the concentrations of the two reactants. The position of the double bond influences the rate of reaction; olefins with an internal double bond react more rapidly than those with a terminal double bond (such as butadiene).

total volume of 1 liter is recommended for personal sampling pumps. One sample of charcoal from each section is transferred to a separate container where each is desorbed for 30 minutes with 1.0 ml of carbon disulfide. An aliquot of each desorbed sample is injected into a gas chromatograph using the solvent flush injection technique. The area of the resulting peak is determined and is then compared with standards based on mg/1.0 ml carbon disulfide; corrections must be made for the blank containing solvent alone.

This method was validated over the range of 1065 to 4590 mg/m³ (coefficient of variation 0.058) at 22°C and 760 mm Hg using a 1 liter sample, although it is probably effective over 200 to 6600 mg/m³. If the desorption efficiency is adequate this procedure could measure smaller amounts. NIOSH cautions that high humidity may decrease the breakthrough volume. Compounds with the same retention time as butadiene at the operating conditions used in this procedure will interfere.

Coker (1977) criticized the NIOSH method, citing several disadvantages: i) on the spot readings are not possible; ii) the pre-analysis procedure is time consuming; iii) desorption solvents (e.g., carbon disulfide) are toxic; iv) solvent peak interferes with the chromatogram; v) recovery is incomplete; and vi) sampling tubes have a limited capacity and cannot be re-used. Coker suggested using heat desorption rather than solvent desorption to overcome these disadvantages. Heat desorption was used successfully to determine butadiene in butenes and butanes from steam cracker units.

Stephens and Burleson (1967) described a chromatographic procedure for analyzing atmospheric light hydrocarbons at concentrations below 1 ppb. A freeze-trap, which was prepared by filling stainless steel tubing with chromatographic substrate was installed in place of the gas sample loop of a flame ionization chromatograph. A sample of 0.1-0.5 liters of air was passed

through the trap; the trap had been chilled with liquid oxygen. The sample was then injected into the chromatograph.

Altshuller et al., (1971) collected samples of light hydrocarbons in California, with an automatic time sequential air sampler. Siddiqi and Worley (1977) sampled hydrocarbons in Texas using a pump or syringe. Both investigators analyzed the samples using a gas chromatograph equipped with a flame ionization detector. Aliphatic hydrocarbons, including butadiene were separated using packed columns.

Manita and Ripp (1965) used spectrophotometric methods to determine small concentrations of 1,3-butadiene in the presence of other compounds (e.g., styrene, isopropylbenzene, butane and butylenes) in the air around a synthetic rubber plant. Air was drawn through silica gel and organic substances were extracted with isooctane. The optical density of the isooctane solution was measured at wavelengths of 224 and 245 nm in a quartz cell with an SF-4 spectrophotometer. For these wavelengths, the Bouger-Lambert-Beer law is obeyed for concentrations of 1-10 micrograms butadiene/ml. The concentration (C) of butadiene (in micrograms/ml) was calculated from this formula:
$$C = 2.5 (E_{224} - 0.47E_{245})$$
; the latter quantity is the difference in absorbance. The sensitivity of this method is 0.125 µg/ml and the accuracy is within ± 2.6%.

Kreuzer et al., (1972) described a method for detecting butadiene and other air pollutants at concentrations of a few parts per billion using gas lasers. The procedure involves measuring the strength of the absorption of infrared radiation at several emission wavelengths from carbon monoxide or carbon dioxide lasers. For butadiene, the absorption was determined at the P(13) line (6,215.3 nm) using the CO laser and at the P(30) line (10,696.4 nm) using the CO₂ laser. Sensitivities of 1 and 2 ppb were obtained with the CO and CO₂ lasers, respectively. This method allows detection of butadiene even in the presence of larger concentrations of other absorbing gases.

b. In Water

Webber and Burks (1952) developed a carbon dioxide stripping method to determine butadiene and other light hydrocarbons in water primarily for the evaluation of hydrocarbon losses in process cooling water and steam condensate. This method involves desorbing the hydrocarbons from water by passing carbon dioxide through the sample; the gas stream is then passed through an absorber and buret filled with a potassium hydroxide solution in which the carbon dioxide is absorbed. The volume of butadiene and other hydrocarbons is measured in the buret as a vapor. In four determinations of known amounts of butadiene in water, the authors reported 93-97% recovery by this method.

Sopach and Krotova (1973) developed, in the U.S.S.R., a method to detect the presence of butadiene in aqueous solutions. This procedure is based on the reaction, in an acetic acid medium, of butadiene with the p-nitro-benzendiazonium ion, which yields a yellow product whose optical density is determined photocolorimetrically. Acetone, toluene, and methylene chloride up to 1,000 mg/liter do not interfere. The sensitivity of the method for butadiene is 2 mg/liter.

c. In Polymers

Residual butadiene monomer in polymer or copolymer by-products can be determined by gas chromatography, either by direct injection or by head-space analysis. Steichen (1976) compared the two methods for butadiene and found solution head-space analysis to be more sensitive (detection limit 0.05 ppm) than direct injection (detection limit 10 ppm). Other advantages of head-space analysis are the prevention of column contamination and the reduction of interferences. Head-space analysis involves the equilibration of a solid polymer in a closed system. The residual monomer is partitioned between the polymer phase and the head-space (air above the sample); the monomer con-

centration in the head-space is then determined. Steichen's (1976) procedure was to equilibrate vials containing butadiene polymer solutions for at least 30 minutes at 90°C before head-space sampling using an automated apparatus.

Shapras and Claver (1964) described a gas chromatographic method for determining residual butadiene in acrylonitrile-butadiene-styrene terpolymer. The polymer was dissolved in chloroform, then dried. A gas chromatograph equipped with a hydrogen flame detector was used to detect less than 10 ppm of residual monomers in styrene-based polymers.

The amount of free butadiene in butadiene rubbers can be determined at >0.005% concentration using a gas chromatograph equipped with a flame ionization detector (LiGotti et al., 1972).

d. In Biological Material

Carpenter et al., (1944) developed a method for determining butadiene in blood based on the reaction with iodine pentoxide. At 200°C, butadiene is completely oxidized by iodine pentoxide, with the liberation of 2.2 molecules of iodine for each molecule of butadiene present. The liberated iodine is collected and titrated with sodium thiosulfate, and the amount is used to calculate the concentration of butadiene. In 8 trials with known amounts of butadiene, recoveries averaged 96.3-99.5% using this method.

e. In Process Streams

Carson, Young and Lege (1972) developed a gas chromatographic column to analyze butadiene plant process streams and the gas phase effluent from naphtha feedstock thermal cracking furnaces in an ethylene plant as well as to analyze commercial grade butadiene. The column consists of two sections connected in series. The first section contains 20% dibutyl maleate and the second contains 10% bis-(2-methoxyethoxy)ethyl ether; both compounds are on 60/80 mesh Chromosorb P-NAW. The column was used on gas chromatographs using

hydrogen flame ionization or thermal conductivity detectors. In Table 31 appears component identification of butadiene process streams (31a) and gas phase effluent (31b) using this column.

The American Society for Testing Materials (ASTM, 1975) described a standard method to detect 1,3-butadiene in C_4 hydrocarbon mixtures. The mixture can contain up to 25% butadiene. The butadiene concentration is calculated from the absorbance of the sample using an ultraviolet spectrometer. Vinyl acetylene and 1,2-butadiene will interfere if present in amounts of 0.5 and 2%, respectively, of the 1,3-butadiene content.

2. Impurities in Butadiene

Carson and Lege (1974) caution that depending on the temperature of the gas chromatographic vaporizer, dimerization of butadiene sample may occur during analysis. This would, therefore, unknowingly increase the amount of dimer reported in the sample. Dimer formation in the gas chromatograph vaporizer varies directly with temperature, as shown in Table 32 for 9 temperature increments between 155 and 325°C. Because of this, the amount of 4-vinylcyclohexene generally reported to be in butadiene may, in fact, be somewhat lower. Vinylcyclohexene can be determined in butadiene concentrates by gas chromatography (ASTM, 1975).

Table 31
Gas Chromatographic Analysis of
A) Butadiene Process Streams and
B) Gas Phase Effluent from an Ethylene
Plant using Naphtha Feedstock
(Carson et al., 1972)

A) Butadiene Process Stream Components

Methane
Ethane + ethylene
Propane
Acetylene
Propylene
Isobutane
Cyclopropane
Propadiene
n-Butane
Neopentane
Butene-1 + isobutylene
Methylacetylene
trans Butene-2
cis Butene-2
1,3-Butadiene
Isopentane
3-Methylbutene-1
n-Pentane
1,2-Butadiene
Ethylacetylene
2 Methylbutene-1
1,4-Pentadiene
trans Pentene-2
Vinylacetylene
2 Methylbutene-2
2-Methylpentane
Isoprene
Dimethylacetylene

Table 31 (Cont'd)
 Gas Chromatographic Analysis of
 A) Butadiene Process Streams and
 B) Gas Phase Effluent from an Ethylene
 Plant using Naphtha Feedstock
 (Carson et al., 1972)

B) Gas Phase Effluent from an Ethylene Plant Using and
 Naphtha Feedstock

Component	Weight %
Air	
Methane	18.73
Ethane + ethylene	35.05
Propane	0.69
Acetylene	0.50
Propylene	19.76
Isobutane	0.04
Propadiene	0.56
n-Butane	0.07
Butene-1 + isobutylene	6.17
Methylacetylene	0.67
trans Butene-2	0.75
cis Butene-2	0.58
1,3-Butadiene	5.95
Isopentane	0.22
3 Methylbutene-1	trace
1,2-Butadiene	0.41
Ethylacetylene	0.29
2 Methylbutene-1	0.69
1,4-Pentadiene	trace
trans Pentene-2	0.21
Vinylacetylene	trace
2 Methylbutene-2	0.44
2 Methylpentane and Isoprene	3.47
Dimethylacetylene	trace

The Ethane-Ethylene Ratio as well as the % hydrogen and carbon dioxide in the above analysis are listed below and were analyzed on other columns.

Component	Weight %
Hydrogen	0.96
Carbon Dioxide	22 ppm
Ethane	5.36
Ethylene	29.69

Table 32
Effect of Temperature on Vinylcyclohexene Formation
in Gas Chromatograph Vaporizer
(Carson and Lege, 1974)

Vaporizer Temperature °C	Dimer PPM	Temperature Increase Above Initial Point °C
155	2	0
170	3	15
185	3	30
200	12	45
215	37	60
230	70	75
245	128	90
260	227	105
275	407	120
300	888	145
325	2,465	170

III. BIOLOGICAL EFFECTS

The available literature on the biological effects of butadiene and its oligomers are discussed in the sections which follow on toxicity and fate. A cursory review of the biological effects of butadiene appears in Parsons and Wilkins (1976).

A. Humans

1. Acute Toxicity

Acute exposures to butadiene are discussed in terms of signs and symptoms, and effects on psychomotor function. No data are available on the toxicity of butadiene oligomers to humans, although their presence has been detected in the workroom of rubber plants (see Section III-A-2).

a. Signs and Symptoms

Inhalation of butadiene is mildly narcotic at concentrations below the lower explosive limit (2% or 44,260 mg/m³) and may result in a feeling of lethargy and drowsiness. Exposure to the gas can cause minor irritation to the eyes and the mucous membranes of the upper respiratory tract as well as asphyxiation by exclusion of oxygen (MCA, 1974; Steere, 1968).

Dermal contact with liquid butadiene causes a sensation of cold followed by one of burning, the result of rapid evaporation; this may cause frostbite. Superficial burns can develop from absorption of butadiene through clothing or skin (MCA, 1974; Lefaux, 1968).

Workers exposed to butadiene vapor in the manufacture of rubber complained of irritation of the eyes, nasal passages, throat and lungs. In some, coughing, fatigue and drowsiness developed (Wilson, 1944). All symptoms disappeared on removal from the vapors. The concentrations were stated only as

"not heavy." Subsequent exposures resulted in the same symptoms, but as these were not excessive, Wilson (1944) suggests there is no cumulative action. Physical and blood examinations and urinalyses were negative.

Two male subjects reported slight smarting of the eyes and difficulty in focusing on instrument scales during 6-7 hours' exposure to 2,000 and 4,000 ppm butadiene (4,420 and 8,840 mg/m³). Exposure for 8 hours to a higher concentration, 8,000 ppm (17,680 mg/m³), was without effect. The authors conclude that butadiene in the concentrations inhaled was innocuous (Carpenter et al., 1944).

Inhalation of a 1% (22,130 mg/m³) mixture of butadiene in air for 5 minutes caused no effects on respiration or blood pressure except for a slight quickening of the pulse, a slight feeling of dryness, and prickling in the mouth and nose. However, 20 exposures for 2 hours each to 140 mg/l (140,000 mg/m³) caused some irritation to the lungs, irritation of the spleen, and slight hyperplasia of the bone marrow (no other details are given) (Von Oettingen, 1940).

A group of 10 or 15 panelists determined eye irritation after exposure to the photooxidation products of butadiene and nitrogen oxide mixtures (Altschuller et al., 1966). Responses were scaled 0-30; the higher the response the more severe the eye irritation. Two indices were calculated: 1) the average response of all panelists; and 2) the average of the highest consecutive responses of all panelists. For the former index, butadiene-nitrogen oxide products scored 20; for the latter, a score of 22 was calculated. These values were higher than eye irritation indices calculated for several compounds, including ethylene-NO and 1-butene-NO mixtures (average responses ranged from 0-13).

Heuss and Glasson (1968) determined the eye irritation of 25 photooxidized hydrocarbons including butadiene. Each hydrocarbon (2 ppm) was added to nitric oxide (1 ppm) in air and the mixture was irradiated in a smog chamber for 6 hours* at 95°F. For butadiene, products yields were: formaldehyde (0.80 ppm); acrolein (0.73 ppm); ozone (0.48 ppm); and peroxyacetylnitrate (PAN, 0.02 ppm). Eye irritation was rated on a scale of 0-3 (0 = none, 3 = severe) after 6 hours by panelists exposed for 4 minutes to reaction products. The time until eye irritation was first detected was also recorded. Of all hydrocarbons tested, photooxidized butadiene was the most severe eye irritant. The time-to-irritation was only 73 seconds; for the other compounds it ranged from 86-240 seconds ($x = 180$ seconds). The photooxidized butadiene containing air was the only mixture rated 3 for the eye irritation index; the other irradiated mixtures ranged from 0.0-2.5 ($x = 1.2$).

The Russian investigator Ripp (1967) studied the effect of butadiene on irritation of the eye in four persons (age 20-35 years). This was determined while the subjects breathed from a cylinder containing pure air and compared to that when butadiene was introduced into the cylinder at 4.2-3.6 mg/m³. At 3.6 mg/m³ there was no change in irritation in any subjects while at 4.2 and 4.0 mg/m³ Ripp reported a "significant increase" in irritation in all subjects. The procedure used to measure irritation was not described.

*The English translation reads "light sensitivity", however, as subjects were exposed in the dark, irritation to the eye was actually being measured.

b. Effects on Psychomotor Tests

Carpenter et al. (1944) evaluated psychomotor responses of two male subjects inhaling, on different days, 2,000, 4,000 or 8,000 ppm butadiene (4,420, 8,840, or 17,680 mg/m³, respectively) for 6-8 hours/day. At the two higher concentrations the subjects performed a steadiness test, while at the highest concentration a tapping rate test was also performed. In the latter test, the number of taps in each 6 second interval of a three minute period were recorded. Results after butadiene inhalation were identical to those obtained before exposure. The steadiness test involved holding at arms length a thin wire in a ring for 3 minutes; the contacts of the wire with the ring were recorded on a kymograph. Results for the steadiness test were inconclusive as the subjects were more unsteady at 4,000 ppm (8,840 mg/m³) (score of 266 compared to 100 for pre-exposure) than at 8,000 ppm (17,680 mg/m³; score of 136). The authors attribute this to the fact that "the subjects were probably physically or mentally below par on the day of the 4,000 ppm test"; i.e., butadiene was probably without effect.

2. Organoleptic Thresholds

The Russian investigator Ripp (1967) determined the olfactory threshold of butadiene to be 4 mg/m³ in 16 persons whose age ranged from 18-36 years.

The following data were obtained in a total of 336 trials:

<u>No. Subjects</u>	<u>Butadiene Concentration (mg/m³)</u>	
	<u>Minimum Perceptible</u>	<u>Maximum Imperceptible</u>
6	4.0	3.8
6	4.2	4.0
3	4.4	4.2
1	4.8	4.4

In addition to odor threshold and light sensitivity, Ripp (1967) also measured the "threshold of reflex action" of butadiene by electrocortical recording. Four persons (2 men, 2 women; 18-30 years old) were exposed to butadiene at 3, 3.6 and 3.8 mg/m³. An electroencephalogram recorded reflex desynchronization of alpha rhythms at the two higher levels tested. Few procedural details were given to enable evaluation of these results.

3. Occupational Exposure

a. Butadiene

Although acute exposure to butadiene may occur through accidents and improper handling, there have been no reports in the U.S. or W. European literature of any chronic effects arising from the industrial use of butadiene. Epidemiologic studies are available for the rubber industry, which is the largest user of butadiene monomer. A number of health hazards have been described for rubber workers. Although the causative agents have not always been identified, butadiene has not been implicated in any of these studies. Suspected or causative agents include the following compounds used in the production of synthetic rubber: styrene, cumene hydroperoxide, p-nitroaniline, phenyl- β -naphthylamine and sodium dimethyl dithiocarbamate (NIOSH, 1976). Some epidemiologic studies have suggested excess morbidity and mortality in rubber workers (Table 33). Among these is the suggestion of excessive mortality from some types of cardiovascular disease, and malignant neoplasms (including, bladder, stomach, large bowel, lymphatic and hematopoietic tissues, and possibly the central nervous and respiratory systems) (McMichael et al., 1977). In the U.S. at least 10 leukemia cases have recently been identified among styrene-butadiene rubber (SBR) workers. (Smith and Ellis, 1977). Since there is no evidence to date in U.S. or Western European literature that butadiene or its metabolites are responsible for excessive disease

Table 33
Epidemiology Studies for Rubber Workers

<u>Job Description</u>	<u>Major Findings</u>	<u>Authors</u>
A. <u>Britain</u>		
rubber workers	differences in morbidity between workers and office staff based on sickness and absenteeism	Parkes, 1966 in McMichael et al., 1976
rubber workers	10% mortality excess compared to national figures	British Registrar General, 1929-31 in McMichael et al., 1976
rubber & cable making industry	excess neoplasms, especially bronchial neoplasms compared to national figures	Fox et al., 1974
	urinary bladder tumors	Case and Hosker, 1954
	higher mortality among production than office workers	Mancuso et al., 1968
B. <u>United States</u>		
rubber workers	increased rate for malignant neoplasms of respiratory system, chronic rheumatic heart disease, emphysema & arthritis compared to other industrial workers	HEW, 1967 in McMichael et al., 1976
rubber workers	excess death rate from malignant neoplasms (8%); chronic rheumatic heart disease (10%); arteriosclerotic heart disease (15%) compared to workers in all manufacturing industries	HEW 1961-1963 in McMichael et al., 1976
tire manufacturers	excess malignant neoplasms of the stomach, prostate and blood-and-lymph forming tissues compared to U.S. national mortality data	McMichael et al., 1976

**Table 33 (Cont.)
Epidemiology Studies for Rubber Workers**

<u>Job Description</u>	<u>Major Findings</u>	<u>Authors</u>
tire curing workers	higher incidence of chronic bronchitis compared to nonexposed rubber workers	Fine & Peters 1976a
rubber processing workers	chronic productive cough compared to nonexposed rubber workers	Fine & Peters 1976b

and mortality, these epidemiologic studies will not be reviewed here (see review in McCormick, 1971).

In contrast to U.S. and Western European investigators, who do not consider butadiene to have chronic toxic effects, Eastern European scientists have recently reported upon effects possibly resulting from occupational exposure to butadiene. A number of studies have been conducted on workers handling butadiene and styrene (or methylstyrene), among other chemicals, during synthetic rubber manufacture. Poorly documented cases of gastrointestinal tract, respiratory, circulatory and nervous system disorders, among others, have been reported. Most of these studies implicate butadiene and styrene as causative agents because they are the basic monomers used in synthetic rubber manufacture. Although such reports also list other major compounds to which workers were exposed, consideration was not usually given to various initiators, modifiers or antioxidants identified by U.S. and Western European investigators as possible health hazards. Many of these studies did not use an adequate control population or provide adequate details of exposure conditions (Scala, 1977). Since workers were exposed to many chemicals, the effects described in the Eastern European literature for rubber workers cannot be attributed to butadiene alone. However, since many of these investigators implicate butadiene as at least one of several possible causative agents, the Eastern European literature is reviewed in the following sections.

Effects on Gastrointestinal Tract and Liver. A Study of 80 workers handling butadiene and styrene during the production of SBR in the U.S.S.R. revealed a higher incidence of chronic gastritis. Changes in the liver included altered detoxification and protein synthesis; changes in the blood protein fractions (decreased albumin level, increased α_1 , α_2 and β globulins) were also observed (Bashirov, 1968). A further study of 130 SBR

workers suffering from chronic gastritis revealed that 73% had accompanying symptoms: inflamed gallbladder (37%), pancreas (17%) and hepatitis (19%) (Bashirov, 1971). These workers were exposed to 0.3-0.5 mg/m³ butadiene and 0.06-0.12 mg/m³ styrene.

Other studies have also reported gastric disorders among workers exposed to butadiene and styrene (Bashirov 1967, 1970, 1973; Batkina, 1966). According to one investigation, exposure to butadiene, styrene, butane, butylene, benzene, sulfuric acid and catalysts produced a high frequency of gastric diseases (66.6%) in a study of 679 synthetic rubber employees. Workers exposed to mixtures of butadiene and styrene showed liver enlargement and a decrease in functional tests of the liver (Quick-Pytel Test) and spinal fluid (Takata-Ara-Test) (Orlova and Solov'eva, 1962).

Volkova et al. (1970) assessed the health of 60 press operators at an SBR rubber vulcanization plant in the USSR based on the following workroom exposures:

	<u>mg/m³</u>
butadiene	26-45
styrene	2-40
oil aerosol	60
formaldehyde	1.1-10
acrolein	1.5
acrylonitrile	1-11
sulfur dioxide, ammonia, carbon dioxide	not specified

Medical examination revealed gastrointestinal tract disturbances, including heartburn, vomiting and nausea (25%), peptic or duodenal ulcers (12%), chronic gastritis (13%), gallbladder inflammation (5%), and liver enlargement (13%).

Effects on the Kidney. A study of 69 workers exposed to butadiene and styrene during synthetic rubber production revealed renal dysfunction in workers with more than 6 years exposure (Konstantinovskaya, 1970). Faustov (1972) also reported kidney dysfunction among synthetic rubber workers, but attributed this (and other toxic effects) to the catalysts used.

Effects on Endocrine Glands. Endocrine function was examined in 70 Russian Styrene-Butadiene Rubber (SBR) workers handling butadiene and styrene; most had been employed for more than 10 years (Bashirov, 1969). The most frequent symptom (34%) was glucocorticoid insufficiency of the adrenal cortex. Thyroid hyperfunction was observed in 24%, while depressed pancreatic activity of the Islets of Langerhans occurred in 20%. The longer a worker had been employed, the more severe the endocrine changes.

Effects on Blood and Circulation. Batkina (1966) reported a tendency to hypotension, leukopenia, and increased erythrocyte sedimentation and hemoglobin levels among 100 rubber workers exposed 10-15 years in areas where butadiene was separated and purified. Khusainova (1971) found the following tendencies among 1,406 workers in contact with butadiene and α -methylstyrene in SBR production compared to 200 controls: increase in hemoglobin, and erythrocytes; leukocytosis; lymphocytosis; decrease in leukocyte glycogen, lipid and peroxidase; decrease in color index.

Functional disorders of the cardiovascular system were reported among workers exposed to butadiene and alpha-methylstyrene (Konstantinovskaya, 1971). In 60 workers having prolonged contact with butadiene, styrene, and ethylbenzene, the following was reported: decreased tonus of the peripheral vascular system (Aleksperov et al., 1971), altered electro - and ballistocardiograms (Aleksperov et al., 1970); abnormal myocardial contraction and hypo-

tension (Vinokurova, 1969); and increased capillary permeability and high resistance to blood flow (Alekperov et al., 1968).

Effect on Lipid-Protein Metabolism. One hundred workers handling butadiene and styrene during rubber production in the U.S.S.R. were examined for adverse effects on lipid-protein metabolism (Lukoshkina et al., 1973). Levels of butadiene and styrene in the workroom air were 85-236.4 and 2-13.5 mg/m³, respectively. Compared to a group of 30 controls, workers exhibited increased blood cholesterol levels (total, free, and esterified), especially as a function of age and length of employment.

Effects on Skin. Of 60 Workers who were exposed to styrene and butadiene and other rubber processing chemicals, 27% showed occupational dermatitis and 33% exhibited mucous membrane changes, including dryness, thickening and pallor (Volkova et al., 1970). Other investigators also noted skin disorders among rubber workers, which include: dry palms (Volkova and Bagdinov, 1969), dermatosis (Mirzoyan and Tsai 1972) and unspecified skin diseases (Abdullaeva, 1973).

Effect on Health & Growth of Juveniles. Klein et al. (1967) compared growth rates and morbidity of 85 apprenticed SBR students with 74 apprenticed agriculture students in Czechoslovakia. The average age of beginning apprentices was 16, and the training lasted 3 years. Although growth rates did not differ, SBR students showed significantly higher rates of infections, illness, and sore throats.

Effects on Nervous System. An examination of 60 workers exposed to butadiene, styrene and other chemicals revealed the following disorders: suppressed corneal (39%) and peritoneal reflexes (31%), and hyperalgesia (30%) (Volkova et al., 1970). Gus'kova (1971) reported adverse effects on the nervous system in workers exposed to butadiene and styrene, and unspecified

"functional disease" of the nervous system were reported among 39% of 100 rubber workers exposed to butadiene (Batkina, 1966).

Effect on Respiratory Tract. A study of 317 workers in a synthetic rubber plant exposed to butadiene, butane, styrene, benzene, sulfuric acid and a catalyst revealed a higher rate of respiratory diseases (18.6% of the workers) among those employed more than 10 years compared to those working less than 5 years (4.25% of the workers) (Abdullaeva, 1973). Faustov (1972) reported inflammation of the mucous membrane among SBR workers exposed to butadiene, styrene, isoprene, solvents and catalysts.

Employees working in a rubber vulcanization area were exposed to butadiene, styrene and other chemicals as well as to heat (Volkova and Bagdinov, 1969). Records of absenteeism were examined and, compared to other workers, there was a high frequency of influenza and catarrh of the upper respiratory tract (26.6%) and tonsillitis (10.9%). Medical examination showed mucosal changes in the upper respiratory tract, which altered olfactory perception. Orlova and Solov'eva (1962) reported laryngotracheitis and bronchitis in workers occupationally exposed to various rubber processing chemicals, including butadiene.

b. Vinylcyclohexene

Russian workers exposed to 4-vinylcyclohexene exhibited keratitis, rhinitis, headache, hypotonia, leukopenia, neutrophilia, lymphocytosis and impairment of pigment and carbohydrate metabolism (Bykov, 1968 in IARC 1976a).

B. Nonhuman Mammals

The available literature on the biological effects of butadiene and its oligomers is discussed in the sections which follow.

1. Toxicology

a. Butadiene

1) Acute Toxicity

a) Lethal Doses.

Butadiene exhibits low toxicity to laboratory animals. In rats, the two hour LC_{50} (concentration lethal to 50% of the organisms) averages 285,000 mg/m^3 . For mice, the 4 hour LC_{50} is 270,000 mg/m^3 . Other lethal concentrations appear in Table 34.

b) Narcotic Effects.

The acute narcotic effect of inhaling high concentrations of butadiene has been described for mice and rabbits in the older literature (Killian, 1930; Larinow et al., 1934 as cited in Von Oettingen, 1940; Carpenter et al., 1944).

In one study, white mice (sex and number used not reported) were exposed to several concentrations of butadiene, ranging from 10 to 40% in oxygen (Killian, 1930). At concentrations of 20 to 40% butadiene, narcosis developed after 6-10 or 0.7-1.0 minutes, respectively. Excitation often preceeded narcosis. The latency to excitation and narcosis is shown in Table 35. Accompanying symptoms included hyperventilation and twitching at 15-30% butadiene. At 40%, all animals died within 11-14 minutes.

Table 34
Acute Lethal Concentration (LC) Values for 1,3-Butadiene

	Lethal Conc. (L.C.) (mg/m ³)	Duration	Reference
Rat ^a	LC ₁₆ = 175,000	2 hr	Shugaev, 1969
	LC ₅₀ = 285,000 (219,000-370,000) ^b	2 hr	Shugaev, 1969
	LC ₈₄ = 460,000	2 hr	Shugaev, 1969
Mouse ^c	LC ₁₆ = 203,000	4 hr	Shugaev, 1969
	LC ₅₀ = 270,000 (251,000-290,000) ^b	4 hr	Shugaev, 1969
	LC ₅₀ = 259,000	N.R.	Batkina, 1968
	LC ₈₄ = 375,000	4 hr	Shugaev, 1969
	LC ₁₀₀ = 300,000	N.R.	Batkina, 1966

N.R. = not reported

^asex; strain, and number tested not given

^b95% confidence limits

^csex and number tested not given by either author; albino mice used by Batkina

Table 35
Effect of Inhaling Varying Mixtures of Butadiene-Oxygen in Mice
(Killian, 1930)

Concentration Butadiene in O ₂ (%)	Time To	
	Excitation (minutes)	Narcosis (minutes)
10	5	-
15	1	-
20	0.5-0.67	6-10
25	-	2-3
30	0.33-0.5	1-1.2
40	-	0.67-1

The Russian investigators, Larionow, Shtessel and Nuselman (1934, as cited in Von Oettingen, 1940) reported that 200,000-300,000 mg/m³ of butadiene is the lowest concentration range necessary to produce narcosis and coma in mice. Irritation of the mucous membranes resulting in conjunctivitis, and nasal and bronchial inflammation were also reported.

Narcotic effects have similarly been described in rabbits. According to Larionov et al. (1934, as cited in Von Oettingen, 1940) exposure to a 25% mixture of butadiene and oxygen caused a loss of labyrinth and motor reflexes but recovery after exposure was rapid. Carpenter et al. (1944) exposed 29 rabbits to this concentration of butadiene in air; symptoms and average time to occurrence are described in Table 36.

Table 36
Effect of Inhaling Butadiene in Rabbits
(Carpenter et al., 1944)

Symptom	Time of Occurrence (minutes)
light anesthesia	1.6
loss of pupillary reflex to strong light	3.8
early pupil dilation	3.9
excitation, running, tremors, chewing	4.6
loss of blink reflex to stimulus	6.5
dry rales	7.1
involuntary blinking	7.4
marked pupil dilation	11.4
death	23.0

In about 9 minutes the butadiene concentration of the blood in the femoral artery was 0.26 mg/ml and in the femoral vein, 0.18 mg/ml. One rabbit survived 34 daily inductions into deep anesthesia with 20-25% butadiene in air without pulmonary damage.

2) Subacute Toxicity

a) Inhalation Exposure.

A short-term exposure study was conducted by Hazleton Laboratories Europe to determine dosage levels for a chronic experiment to be sponsored by ISSRP (International Institute of Synthetic Rubber Products) (Scala, 1977). Groups of 40 male and 40 female rats were exposed to atmospheres containing 0, 2200, 4400, 8800 or 18000 mg of butadiene/m³ for 6 hours/day, 5 days/week over 13 weeks. The concentration of butadiene dimer (4-vinylcyclohexene) in the 18,000 mg/m³ exposure group ranged from 3.32-11.05 mg/m³. There were no signs of toxicity attributable to butadiene at any concentration tested. A dose-related decrease in grooming behavior, associated with discolored hair-coat and, in some cases, discolored saliva, occurred after 8 weeks' exposure. Another effect was a change in neuromuscular function (as measured by a rotating spiral test) in males at the low exposure level (2,200 mg/m³) and in females at 2,200 and 4,400 mg/m³. The changes in the two sexes were in the opposite direction and did not occur at the high doses; the biological significance of these data was called "questionable" by Scala (1977). Scala also attached no "biological significance" to the increase in red blood cell cholinesterase activity in all test groups seen at 2, 6, and 13 weeks. Another finding was a reduction in brain cholinesterase activity in males at the two highest levels. In females, receiving the highest dose, the absolute level of brain cholinesterase was elevated; however, tissue examination revealed spontaneous disease rather than evidence of butadiene-induced effects.

The effects of inhaling much lower levels of butadiene have been described in a series of papers appearing in the Russian literature. Groups of 14-15 male albino rats were exposed to butadiene at concentrations of 0 (pure air), 1.07 ± 0.006 , 3.08 ± 0.006 , or 30.8 ± 0.075 mg/m³ for 24 hours/

day for 81 days. Animals at each exposure level were intoxicated as a group in 0.1 m^3 chambers; the butadiene concentration in the chambers was checked daily via spectrophotometry. Ripp (1967) described gross and microscopic effects; data were supplemented by papers on spleen changes (Molodyuk, 1969), and on hepatic and cardiac effects (Nikiforova et al., 1969). A reiteration of these results appears in Ripp (1969). The changes observed in rats during and after exposure to butadiene for 81 days are described in the 7 subsections which follow:

Effects on Demeanor and Weight. Rats exposed continuously to 30 mg/m^3 displayed "a certain unrest" during the first days of intoxication. By the end of the third month, activity was reduced. Animals receiving lower levels of butadiene (1 or 3 mg/m^3) behaved within normal limits (Ripp, 1967).

Weight gain was normal for rats exposed to 1 and 3 mg/m^3 , and rats exposed to 30 mg/m^3 gained weight normally until about day 50; after this time, weights decreased until the end of the experiment (day 81). Weights at the beginning and end of the experiment were as follows:

Group (mg butadiene/ m^3)	Day 0 (g)	Day 81 (g)	% Increase
0	170	258	51.8%
1	175	248	41.7%
3	172	245	42.4%
30	175	230	31.4%
(extrapolated from graph in text)			

Effect on Blood Indices. Evaluations were made every 2 weeks on 5 rats/group for erythrocytes, reticulocytes hemoglobin, and leukocytes. All values were within normal limits except for a statistically significant increase in the leukocyte count on day 80 in rats exposed to 30 mg/m^3 . No data were presented to support this claim.

Effect on Cholinesterase. The time (in minutes) for acetylcholine to be hydrolyzed was used to measure whole blood cholinesterase activity. Determinations were made prior to intoxication and every two weeks during intoxication on 5 rats/group. The results are presented in Figure 10. Only in rats inhaling butadiene at 30 mg/m^3 was cholinesterase activity increased; this level returned to normal after cessation of treatment.

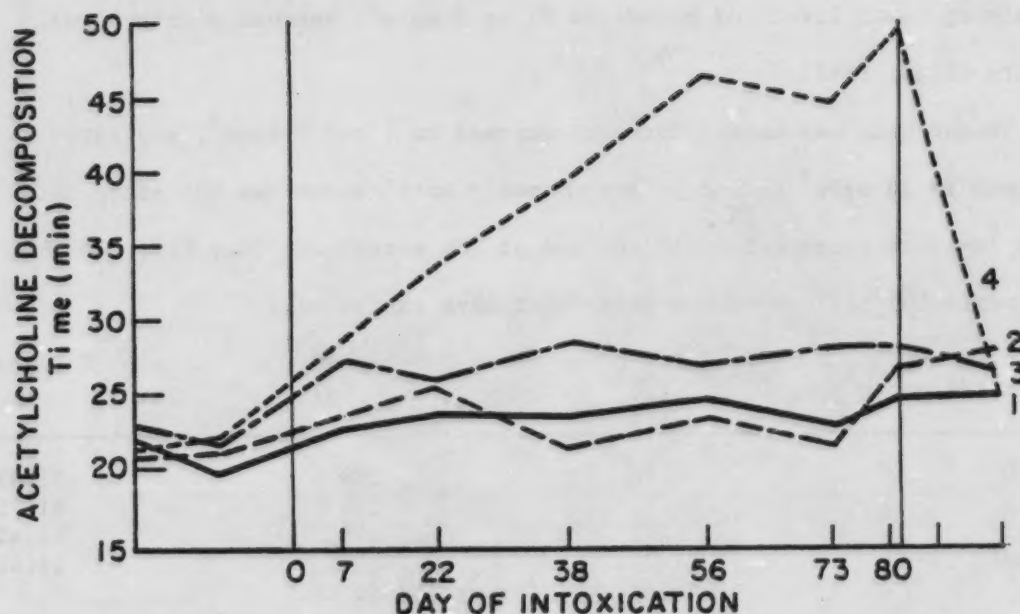


Figure 10. Effect of Butadiene on Cholinesterase Activity of Whole Blood of Rats Exposed Continuously to Butadiene for 81 Days. Group 1) control; 2) 1 mg/m^3 ; 3) 3 mg/m^3 ; 4) 30 mg/m^3 (Ripp, 1967)

Effect on Optic Properties of Blood Serum. As a determination of serum protein, the optical properties of blood serum were measured. The absorption index (optic density) of the serum increased in rats exposed to 30 mg/m^3 (pre-intoxication index, 1.7-1.85; day 30 index, 2.03-2.36), but not in rats exposed to lower levels of butadiene. The position of the absorption bands of the blood serum did not change in any group.

Effect on Arterial Pressure. Arterial pressure of the tail was measured in 5 rats/group (using a sphygmomanometer) every three weeks during intoxication. Arterial pressure was stable in all groups for about 2 months. However, on the 72nd day of intoxication the arterial pressure in rats exposed to 30 mg/m^3 declined and remained at this level until the end of treatment and during the recovery period (Figure 11).

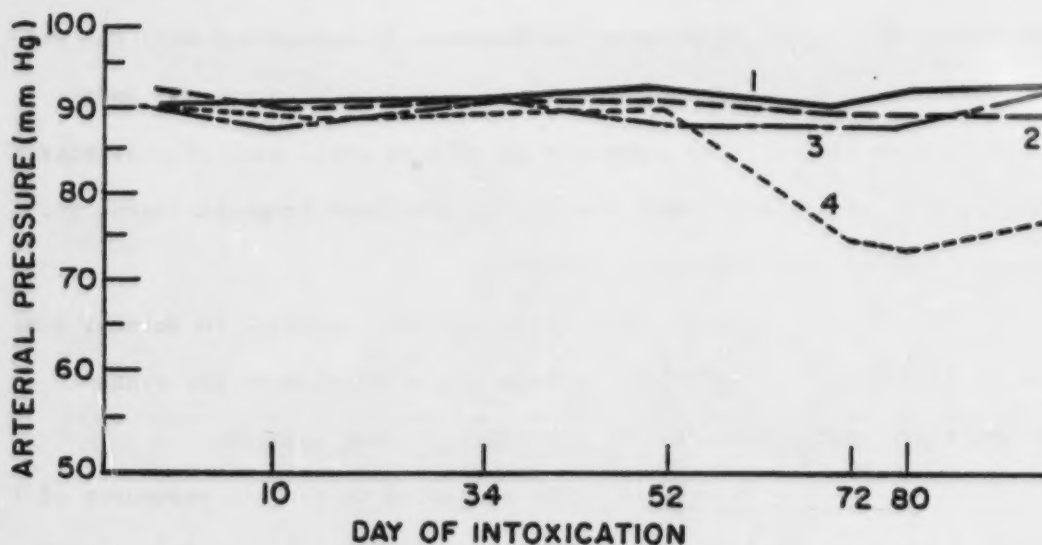


Figure 11. Effect of Butadiene on Blood Pressure of Rats Exposed Continuously to Butadiene for 81 days.
Group 1) control; 2) 1 mg/m^3 ; 3) 3 mg/m^3 ; 4) 30 mg/m^3
(Ripp, 1967)

Effect on Motor Activity. The motor activity of 5 rats/group was recorded during 3 hour periods several times per week in special chambers to electronically score movement. The motor activity was unchanged in rats exposed to butadiene at 1 and 3 mg/m³ for 81 days. However, activity decreased to 60% of pre-exposure activity after seven weeks in rats exposed to 30 mg/m³.

Effects on Tissues and Organs. After 81 days of exposure, tissue sections of liver, kidney, heart, spleen, brain and bone marrow were examined. In all rats the mucous membrane was not intact to some extent; Ripp (1967) suggests this was the result of "environmental factors" such as crowding, air, humidity, etc. Other changes were dose-dependent and are described below for each organ examined.

Lung. All rats inhaling butadiene showed some changes in the lung. At 1 mg/m³ there were "differences in comparison with the control", however, no other details were given. At 3 mg/m³ there was moderately pronounced interstitial pneumonia as well as small foci of atelectasis and emphysema. At 30 mg/m³ there was highly developed lymphoid tissue and also small foci of atelectasis and emphysema.

Liver. No alterations were apparent in animals subjected to 1 or 3 mg/m³. At 30 mg/m³ there was a thinning of the trabeculae and almost total absence of light cells in some animals.

Spleen. In rats subjected to chronic exposures of 1 mg/m³, the spleen contained an excess of erythrocytes. At 3 mg/m³, abnormal changes in the spleen included: indistinct nuclei of the connective tissue; plethora of vessels; and a reduction of RNA. More distinct changes occurred in rats inhaling 30 mg/m³. The vessel endothelium was swollen;

vessels and sinuses revealed small hemorrhages and were plethoric. Distributed throughout the follicles were reticular cells, lymphoblasts, and macrophages. In addition, the capsules and trabeculae were loosened and the lymphoid follicles were enlarged.

Kidney. Continuous inhalation of 1 mg/m^3 of butadiene for 81 days resulted in no visible ultrastructural alterations in the kidneys; however, at 3 mg/m^3 , butadiene induced these changes: loosening of the capsule; accumulation of connective tissue cells; excessive hyperemia of the glomerular capillaries; and in some cases, deformation of the epithelial cell nuclei in the convoluted tubules. Renal changes were more pronounced at 30 mg/m^3 . These included 1) loosening of the adipose capsule and hyperemia, 2) swelling or enlargement of the glomerula, capsules, lumen and convoluted tubular epithelia, 3) proliferation of connective tissue, fibroblasts, macrophages and plasma cells in some areas of the kidney and 4) reduction in the RNA level of some tissues.

Heart. Chronic inhalation of butadiene at 1 mg/m^3 resulted in no visible structural alterations of the muscular fibers of the heart, but some areas of the vessels were hyperemic and infiltrated by leukocytes. The heart of rats inhaling 3 mg/m^3 exhibited reduced differentiation of the endothelium, deformation of endothelial nuclei, and capillary hyperemia and hemostasis. Rats exposed to 30 mg/m^3 exhibited cardiac hyperemia, hemostasis and hemorrhage; in addition, the RNA level of cell cytoplasm was reduced.

b) Oral Administration.

Tissue and organ changes were observed in 25 rats (sex and strain not specified) receiving daily oral doses of butadiene of 100 mg/kg in vegetable oil for 2.5 months; 10 control rats received vegetable oil only (Donetskaya

and Shvartsapel, 1970). Histological and histochemical sections revealed degenerative, sometimes necrotic, changes in the cytoplasm of cells of the heart, liver, kidneys, nervous tissue and vascular walls. These cytoplasmic changes included granular and hydropic dystrophy, cytolysis, neuronophagia, and altered vessel permeability. The authors state that these changes are related to butadiene "to a certain degree"; whether these changes also occurred in control animals is not clearly stated. Some circulatory changes, however, were stated as likely due to butadiene: venous hyperemia, stasis, hemorrhage, and edema; these changes were more pronounced in experimental animals. The authors consider the following changes not due to butadiene administration, as controls also exhibited these abnormalities: hyperplasia of hepatic reticular tissue; proliferation of alveolar epithelium; and infiltration of lymphocytes in the heart, liver, kidneys, gastrointestinal tract and subcutaneous tissue. The absence of more detailed data limit the usefulness of this Russian study.

3) Chronic Toxicity *

Published studies on the chronic effects of butadiene have appeared in the U. S. and Russian literature. In addition a long-term study is currently underway at Hazleton Laboratories Europe (sponsored by the International Institute of Synthetic Rubber Producers). In this investigation, groups of 110 male and 110 female rats are being exposed to butadiene at 0, 2200, or 18000 mg/m^3 for 6 hours/day, 5 days per week for 24 months. No results are available at this time.

a) Inhalation Exposure.

In a chronic exposure experiment in the U.S.S.R., Batkina (1966) exposed albino rats and rabbits (no sex, species, or number given) to butadiene at 10, 100 or 2,000 mg/m^3 for 4 hours/day for 4 months. Rats previously trained to respond to sound showed a slower reaction time after long-term exposure to

*defined here as exposure for 90 or more days

butadiene; the time-to-response was 0.33 seconds in controls, 1.04 seconds in the 100 mg/m³ group and 0.74 seconds in the 2,200 mg/m³ group. Hematological changes observed included reduced leukocyte counts (40% lower in rats given 2,200 mg/m³) and alterations in serum protein (Table 37). In rabbits, chronic exposure resulted in inhibition of serum cholinesterase at the two higher levels (Table 38), as well as a decrease in the phagocytic activity of neutrophils. In both rats and rabbits, chronic exposure to 10 mg/m³ was without effect (Batkina, 1966).

The U. S. investigators Carpenter et al. (1944) exposed laboratory animals to higher concentrations of butadiene for longer periods of time than did Batkina (1966). A total of 164 rats, guinea pigs, rabbits and dogs were exposed in a dynamic chamber to butadiene vapors at 600, 2300 or 6700 ppm (1326, 4830, 14807 mg/m³) for 7.5 hours/day, 6 days/week for 8 months; controls were exposed to air only. An equal number of males and females were used, except for dogs (females only). Several parameters were considered, as summarized in Table 39 and described below in the four subsections which follow.

Growth and General Health. There were no deaths among experimental animals that could be attributed to butadiene. About 5% of exposed rats developed "some extraneous infections", but these were not considered significant. For rats and guinea pigs, exposure to butadiene affected weight gain in a dose-related manner. At the termination of the experiment, weights of rats were 90.5, 86.3 and 81.2% of the controls for the 1326, 4830 and 14807 mg/m³ groups, respectively; no comparable data for guinea pigs were presented. However, the four female dogs were heavier at the termination of the experiment for all exposures.

The ratio of body weight to body weight was determined for rats only. Final ratios were 4.3, 8.7 and 14.8% less than controls for the 1,326, 4,830 and 14,807 mg/m³ groups. The authors considered this variation normal.

Table 37
Serum Protein in Rats after Chronic Exposure
(4 hours/day, 4 mo.) to Butadiene
(Batkina, 1966)

	Control	Concentration of BD		
		2200	100	10
Total Protein	7.52 ± 0.17	8.72 ± 0.17*	8.01 ± 0.27	8.31 ± 0.33*
Albumins (g%)	2.81 ± 0.14	4.25 ± 0.20*	3.78 ± 0.17*	3.58 ± 0.26*
α ₁ -globulin	1.01 ± 0.04	0.72 ± 0.15*	0.75 ± 0.10	0.88 ± 0.13
α ₂ -globulin	0.71 ± 0.02	0.67 ± 0.11*	0.59 ± 0.06	0.72 ± 0.02
β-globulin	1.48 ± 0.051	1.52 ± 0.15	1.44 ± 0.15	1.58 ± 0.19
γ-globulin	1.40 ± 0.04	1.43 ± 0.21	1.33 ± 0.19	1.41 ± 0.20
Lipoproteins (g%)				
α	12.2 ± 0.58	9.7 ± 0.83*	9.4 ± 0.89*	11.3 ± 1.23
β	29.9 ± 1.09	56.4 ± 2.05*	43.3 ± 1.99*	49.3 ± 3.38*
γ	57.9 ± 1.37	33.9 ± 2.47*	47.3 ± 2.16*	39.4 ± 3.50*

* p < .05

Table 38
Serum Cholinesterase Activity in Rabbits after
Chronic Inhalation Exposure (4 hours/day,
4 months) to Butadiene (Batkina, 1966)

Concentration	X % decomposed Acetylcholine	p ^a
0 (Control)	16.4	
2200	11.98	<0.05
100	11.94	<0.05
10	13.76	>0.05

^athe author calculated P using a t-test, which, however, should not be used on percentages.

Table 39
Effects of Chronic Inhalation of Butadiene by Rats,
Rabbits and Guinea Pigs (7.5 hours/day,
6 days/week for 8 months)^a
(Carpenter et al., 1944)

Parameter ^b	ppm (mg/m ³)	Response/Exposure Group			
		0	600	2,300	6,700
		0	1,326	4,830	14,807)
Deaths attributable to exposure for all species		0	0	0	0
Weight at 8 mo. as % of control for rats		-	90.5%	86.3%	81.2%
Weight at 8 mo. as % of starting weight for dogs		104.4%	111.1%	108.0%	114.7%
Ratio of body length to body weight at 8 mo. as % of control for rats		-	95.7%	91.3%	85.2%
Kidney weight for rats		normal	normal	normal	normal
Liver weight for rats		normal	lower than control	lower than control	normal
Blood counts and clinical chemistry for rats		normal	normal	normal	normal
Litters/female for rats		3.3	2.72	2.5	2.62
Young/litter					
rats		7.8-7.9	8.4	7.9	7.8
guinea pigs		16	13	10	13
rabbits		24	(no litter)	(no litter)	27
Pathology of adrenal, heart, kidney, skeletal muscle, pancreas, spleen, testis or ovary for all species		none	none	none	none

Table 39 (Cont.)
Effects of Chronic Inhalation of Butadiene by Rats,
Rabbits and Guinea Pigs (7.5 hours/day,
6 days/week for 8 months)^a
(Carpenter et al., 1944)

Parameter ^b	ppm (mg/m ³)	Response/Exposure Group			
		0	600	2,300	6,700
		0	1,326	4,830	14,807)
Pathology of eye for dogs and rabbits		none	none	none	none
Cloudy swelling of liver for all species (%)	10	-	-	-	68
Congestion of liver for all species		sporadic	sporadic	sporadic	sporadic
No. instances fatty infiltration of guinea pigs	0	1	2	0	
Congestion of lung for all species		yes, very frequent	yes	yes, but not frequent	yes

^a exposure in chamber to a total of 164 animals; four groups of 24 albino rats, 12 guinea pigs, 4 rabbits, and 1 dog.

^b data as given in original reference; no additional information available (i.e., a parameter labeled "normal" here was so identified in text).

At the end of the exposure period, kidney and liver weights of rats were determined. Kidney weights were within normal range for all groups. The liver weights for the 1,326 and 4,830 mg/m³ groups were "slightly lower" than those of controls but those of the 14,807 mg/m³ group were normal. The authors attribute these differences to the uncertainty inherent in the method of sacrifice used (cord sectioned then bled completely). No data on kidney or liver weights were presented.

Effects on Blood. Monthly blood counts on all animals revealed no abnormalities with respect to hemoglobin, erythrocyte, leukocyte or differential counts. For rats and dogs, clotting time, reticulocyte count and white cell volume were also determined and found to be within the normal range.

At the end of the experiment, blood urea nitrogen and bilirubin were normal in all animals. Urinalyses for albumin, sugar and casts were likewise normal.

Effects on Fertility and Reproduction. The number of litters per female and the number of young per litter were both used as indices of fertility in rats. Butadiene affected the former measurement only. Disregarding infertile females, the number of litters per female during the experimental period was 3.3, 2.72, 2.5 and 2.62 for the 0, 1,326, 4,830 and 14,807 mg/m³ groups, respectively. The number of young per litter, however, was unaffected and actually increased in one case: 8.4, 7.9, 7.8, pups/litter for the 1,326, 4,830 and 14,807 mg/m³ groups, respectively; the control average was not stated specifically but ranged between 7.9-7.8. For guinea pigs and rabbits only the number of young per litter was determined, and was found to be within normal limits (Table 38).

Pathology. The eyes of dogs and rabbits were examined grossly during the course of exposures and microscopically after killing. No

abnormalities were found in the cornea, sclera, retinal ganglion cells, optic nerve or other retinal layers.

No pathological changes occurred in the adrenal glands, heart, kidneys, skeletal muscle, pancreas, spleen, testes or ovaries. Both experimental and control animals exhibited lung congestion. Liver congestion was probably a response to butadiene: 68% of all animals in the 14,807 mg/m³ group showed light cloudy swelling compared to 10% in controls. Fatty infiltration occurred in the livers of 3 exposed guinea pigs (2 from the 4,380 mg/m³ and 1 from the 1,326 mg/m³ group).

b) Oral Administration

The Russian investigator Shvartsapel (1970) administered butadiene to rabbits by gavage in a chronic experiment. A total of thirty-six rabbits (sex and strain not given) were given doses of 0.4, 4.0 or 40 mg/kg body weight of butadiene in vegetable oil for 7 months (the dose schedule was not specified); controls received vegetable oil only. Several parameters were measured every month during intoxication: whole blood free sulfhydryl (SH) concentration, serum acetylcholinesterase, cholinesterase and fructose-diphosphate aldolase activities, and hemoglobin level. Shvartsapel (1970) observed no changes for the first three parameters in experimental rabbits (no data are presented). In rabbits receiving 40 mg/kg, there was a significant increase in the activity of the enzyme fructose-diphosphate aldolase during the seventh month, and a slight decrease in hemoglobin after the fourth month. Rabbits receiving lower butadiene doses were unaffected (Table 40).

Table 40
Chronic Feeding of Butadiene to Rabbits for 7 Months:
Effect on Serum Fructose-Diphosphate Aldolase (FD)
Activity and Hemoglobin (Hb) (Shvartsapel, 1970)

Month	Dose (mg/kg bw)							
	0	0	0.4	0.4	4.0	4.0	40.0	40.0
	FD ^a	Hb ^b	FD	Hb	FD	Hb	FD	Hb
0	22.84	11.45	22.18	11.6	23.28	12.01	24.10	11.16
1	23.63	12.54	23.81	12.24	23.22	12.19	23.24	12.00
2	21.48	13.27	21.91	13.12	22.83	12.86	23.72	12.92
3	26.91	12.48	23.45	11.21	28.67	12.74	26.60	12.40
4	24.98	13.0	24.16	13.00	23.78	12.91	24.61	12.56
5	23.34	13.0	23.89	12.92	22.93	13.06	24.46	12.60
6	27.39	12.88	28.56	12.99	25.91	12.48	34.96	12.57
7	27.46	12.41	28.39	12.48	30.97	12.11	38.30	11.67

^a fructose-diphosphate aldolase activity; the units of measurement are unclear, as a translation from the Russian yields "TB" units, for which no English equivalent was found.

^b hemoglobin expressed in g%

b. Butadiene Containing Mixtures

Reports are available in the Russian literature on the toxicity of butadiene mixed with one or more compounds. Observed effects, therefore, are not necessarily due to butadiene. For completeness, these studies are included, but will be discussed only briefly.

1) Butadiene- α Methylstyrene (BD-MS)

A series of Russian studies are available on the effects of chronic inhalation of butadiene- α -methylstyrene mixtures. Rats were exposed to these mixtures for 4 months and the resulting effects were evaluated in several organ and tissue systems by a number of authors. One study is discussed in detail below, followed by a summary of the effects found in similarly exposed rats.

Padeeva and Eikhler (1971) reported altered blood-values, oxidation-reduction reactions, and metabolism as a result of chronic inhalation of butadiene- α -methylstyrene. Male albino rats inhaled mixtures 6 hours/day,

6 days/week for 4 months. A total of 42 rats was used in 3 experimental groups:

- 1) controls, exposed to air only
- 2) mixture of $47.9 \pm 2.9 \text{ mg/m}^3$ butadiene and $2.88 \pm 0.2 \text{ mg/m}^3$ α -methylstyrene
- 3) mixture of $99.8 \pm 4 \text{ mg/m}^3$ butadiene and $5.2 \pm 0.3 \text{ mg/m}^3$ α -methylstyrene

In rats exposed to the higher level only, the leukocyte and phagocyte count in the blood and the cholinesterase activity in the blood were reduced from the control (Table 41).

Blood free sulfhydryl (SH) content at the higher dose was increased 300 to 400 micromoles/100 ml over control values by the end of the second month; this elevation was maintained to the end of the experiment and for 2 weeks after cessation of treatment. At the lower dose, free SH increased, but to a lesser degree.

To study the effect of butadiene- α -methylstyrene on oxidation-reduction reactions, urine coproporphyrin elimination was measured from 5 rats in each group. After the fourth week there was a significant increase in coproporphyrin elimination in both experimental groups; however, no data were presented to support this statement.

As a measure of metabolism, the levels of various vitamins were determined. Beginning after 80 days, rats receiving the higher dose showed a significant increase in the amount of ascorbic acid in the urine and a tendency toward reduced levels in the blood (no supporting data were presented). At the end of the 4 months, rats given the larger dose showed decreased levels of ascorbic acid in the liver and brain and also a decreased amount of vitamin B in the liver (Table 41). There were no changes in the vitamin levels

Table 41
Effect of Chronic Inhalation of Mixtures of
Butadiene-Alpha-Methylstyrene in Rats^a
(Fadeeva and Eikhlor, 1971)

	Control	47.9 butadiene + 2.88 methylstyrene (mg/m ³)	99.8 butadiene + 5.2 methylstyrene (mg/m ³)
Leukocyte Count			
Day 0	14,779 ± 2173	same as control ^b	15,550 ± 1314
Mo. 4	same level as above ^a	same as control ^b	9,925 ± 1375
Phagocyte Count^c			
Week 6	3.02	3.53	3.60
Week 7	3.22	3.42	3.17
Week 8	3.32	3.38	2.96
Week 9	3.52	3.30	2.54
Week 10	3.62	3.26	2.32
Cholinesterase Activity (micromoles of hydrolyzed acetylcholine)			
Day 10	1.448 ± 0.074	-b	1.578 ± 0.037
Day 20	1.397 ± 0.094	-b	1.085 ± 0.103
Mo. 4	1.482 ± 0.067	same as control ^b	1.319 ± 0.027
Ascorbic Acid (mg %)			
Liver, mo. 4	36.2 ± 1.98	-b	31.3 ± 0.84
Brain, mo. 4	20.6 ± 1.27	-b	15.0 ± 1.30
Vitamin B (mg %)			
Liver, mo. 4	2.27 ± 0.17	-b	1.78 ± 0.7

^a exposed 6 hours day, 6 days/week, 4 months

^b data not given in original text

^c data smoothed by method of least squares

of these tissues in rats receiving the lower dose. For both experimental groups no changes were detected in hemoglobin or nuclei acid levels in the blood or in body weight throughout the experiment.

Additional effects have been noted by a number of other authors in rats inhaling up to 100 mg/m^3 butadiene and alpha-methylstyrene mixtures for four months (6 days/week). Some changes were time dependent, as summarized below:

days 10-30 - myeloid, lymphoid and erythroblastic reactions observed in bone marrow, lymph glands, and spleen (Molodyuk, 1969).

- in females, the number of primordial and maturing follicles decreased; the number of eosinophils in the mucous membrane of uterus increased (Morozov, 1969a).

- alteration of the bronchial epithelium, increased permeability of blood vessels (Kuz'min, 1969).

day 60 - mature elements of bone marrow were larger; lymphopoiesis was inhibited in lymph glands and spleen (Molodyuk, 1969).

- restoration of spermatogenesis (Morozov, 1969b).

days 90-120 - blood cell composition began to normalize (Molodyuk, 1969) in males, inhibited spermatogenesis (Morozov, 1969b).

Other effects were observed at the end of the experimental period including: a reduction in the number of neutrophils and in serum proteins, and an increase in α_2 -globulins (Matusov, 1969); an increase in blood and liver cholesterol (Chukreev, 1969); a decrease in the permeability of blood vessels (Kuzmin, 1969); a decrease of liver glycogen, accumulation of lipids in liver cells and redistribution of total liver protein (Lambina, 1969a and b); symptoms similar to protein dystrophy of the kidneys (Serebrennikov, 1969); and disturbed hemodynamics (Bul'Bakov, 1969).

2) Butadiene-Toluene

Inhalation for 2 hours of a combination of butadiene (100 mg/l) and toluene (20 mg/l) resulted in a prolongation of estrous in female rats previously cycling regularly. Chronic exposures to lesser amounts (0.1 mg butadiene/l and 0.05 mg toluene/l, 3-6 hours/day for 2 months) resulted in similar lengthening; normal estrus was restored in 50% of the rats 5 months after termination of treatment (Skuja, 1969).

Exposure of rabbits to a mixture of butadiene and toluene 4 hours daily for two months caused changes in the bone marrow and serum; the total protein content decreased and the ratio of albumin to globulin increased (Faustov and Lobeeva, 1970).

c. Vinylcyclohexene

1) Acute Toxicity

Smyth et al. (1969) measured several parameters of toxicity for 4-vinylcyclohexene (summarized in Table 42). In rats, the acute oral LD₅₀ value was determined to be 3.08 ml/kg (equivalent to 2,556 mg/kg)*. Rats can inhale "concentrated" vapors for a maximum of 15 minutes before death occurs. Inhalation of 8,000 ppm (35,360 mg/m³) for 4 hours resulted in 67% mortality (6 animals tested).

For rabbits, the single skin penetration LD₅₀ was 20 ml/kg (16,598 mg/kg) when retained beneath plastic film, contacting the skin for 24 hours. Vinylcyclohexene caused irritation to the uncovered rabbit belly within 24 hours (graded "4" on a scale of 1, no reaction to 10, necrosis). When applied to the cornea of rabbits, it produced a mild reaction (graded "2" on a scale of 1, slight reaction to 10, severe reaction).

*conversion based on density of vinylcyclohexene (0.8299)

Table 42
Range-Finding Toxicity Data for 4-Vinylcyclohexene
(Smyth et al., 1969)

<u>Item</u>	<u>Data</u>	<u>Method</u>
Acute Oral LD ₅₀ for rats	3.08 ml/kg; range 2.49-3.81 (2,556 mg/kg)	Administered to groups of 5 Carworth-Wistar male rats (90-120 g) by gavage, observed for 14 days
Acute Dermal LD ₅₀ for rabbits	20 ml/kg (16,598 mg/kg)	Fur clipped in groups of 4 male albino New Zealand rabbits (2.5-3.5 kg) and VCH retained beneath plastic film contacting skin for 24 hr; observed for 14 days
Concentrated vapor inhalation by rats, Maximum time for no death	15 min.	Groups of 5 male or female albino rats exposed for varying time intervals
Inhalation of 8,000 ppm (35,360 mg/m ³) for 4 hours	mortality: 4/6	Exposure of 6 rats in inhalation chamber; observed for 14 days
<u>Topical application:</u> Uncovered rabbit belly	4	Reaction within 24 hours in 5 albino rats; Grade 1 - no reaction, Grade 10 - necrosis from 0.01% solution
Rabbit cornea	2	Reaction Graded 1 - slight reaction to 10 - severe reaction

2) Chronic Toxicity

Inhalation of 1,000 mg/m³ of 4-vinylcyclohexene for 6 hours/day over 4 months inhibited weight increase and caused leukocytosis, leukopenia and hemodynamic impairment in rats and mice (Bykov, 1968 in IARC, 1976a).

Long-term skin application in mice is described in the next section.

3) Carcinogenic Potential

Vinylcyclohexene was tested for carcinogenicity by skin application in male Swiss-Millerton mice, as discussed in the carcinogenicity section (IV-B-3). Because testing was only by skin application, the International Agency for Research on Cancer stated that it is not possible to evaluate carcinogenicity in vinylcyclohexene. The National Cancer Institute plans to begin a carcinogenesis bioassay on vinylcyclohexene in October 1978 (Chase, pers. comm., 1978).

d. Cyclooctadiene and Cyclododecatriene

Brown and Hunter (1968) tested the dermal toxicity of 1,5-cyclooctadiene and 1,5,9-cyclododecatriene. The samples tested consisted of 98% w/w of the cis,cis-isomer of cyclooctadiene with 0.02% 2,6-diterbutyl-4-methylphenol added as a peroxide inhibitor. The cyclododecatriene sample contained 90% cis,trans,trans-isomer with 0.1% of the same inhibitor. Both samples caused severe contact dermatitis in laboratory mammals in several tests, as described in the three subsections which follow.

Skin Irritation Study. Rabbits were tested in a "covered test". The compounds were applied on shaved skin using a 2 x 2 cm bandage, which was then covered with a sheet of polythene. The bandage was in place for 6 hours/day for 3 successive days. Epidermal sloughing was especially apparent after the application of cyclooctadiene; the skin was grossly injured.

A post mortem examination revealed necrosis of the epidermis, and ulceration and inflammation of the dermis with cyclooctadiene. Following cyclododecatriene application, there were acanthosis and a proliferative epidermal reaction.

In an "uncovered test", the samples were applied on shorn skin of rabbits, guinea pigs and hairless mice daily for 4-5 weeks (5 days/week). With cyclooctadiene, an immediate erythematous reaction was noted in all species after the first application, followed by acute contact dermatitis and epidermal sloughing. For cyclododecatriene, severe contact dermatitis occurred. Ulceration was observed in one mouse on histopathological examination. Guinea pigs killed 3 weeks after the last application of the compounds showed epidermal thickening and considerable acanthosis.

Skin Sensitization Studies. Tests were carried out by topical application and intradermal injection of a 0.1% w/w solution of the test compounds in light liquid paraffin. This procedure was performed 3 days/week for 3 weeks on the backs of guinea pigs, followed by no treatment for 10 days. Then the test compound was administered again. The animals were examined at 24 and 48 hours. Most animals showed sensitization, as indicated below (no data for controls are given):

	No. Guinea Pigs Showing Positive Reaction/No. Guinea Pigs Tested			
	Topical Test		Intradermal Test	
	24 hr	48 hr	24 hr	48 hr
Cyclooctadiene	10/10	10/10	9/10	9/10
Cyclododecatriene	10/10	10/10	10/10	10/10

Eye Tests. When applied to the eyes of rabbits, both cyclooctadiene and cyclododecatriene caused immediate irritation and conjunctivitis, which faded within 48 hours. The eyelids became red and swollen and exuded a purulent discharge. Both compounds caused blepharitis; this condition healed in a few days after application of cyclooctadiene but persisted for a week or more after cyclododecatriene treatment.

2. Biological Fate

Few studies are available on the absorption, distribution or biotransformation of butadiene or its oligomers.

a. Butadiene

1) Absorption

The distribution coefficient of butadiene *in vitro* between rabbit blood and air averaged 0.603 (range 0.555-0.662) at 37.5°C and 760 mm pressure in 5 determinations. *In vivo*, the distribution coefficient averaged 0.654 (range 0.535-0.801) in 10 determinations. Since there is good agreement between *in vivo* and *in vitro* blood distribution coefficients, Carpenter et al. (1944) suggested that the passage of butadiene from inspired air into the blood is a process of simple diffusion of gas from the alveoli of the lungs.

2) Distribution

Carpenter et al. (1944) determined the level of butadiene in blood after inhalation exposure. In rabbits exposed to 250,000 ppm butadiene (552,500 mg/m³), the concentration of butadiene in the blood after 9 minutes was 0.26 mg/ml in the femoral artery and 0.18 mg/ml in the femoral vein.

A Russian investigator, Shugaev (1969), measured the distribution of butadiene in several tissues after inhalation exposure, using gas-liquid chromatography. Rats (strain or sex not given) exposed to 285,000 mg/m³ for 2

hours (LC_{50}) showed a high concentration of butadiene in the perinephric fat (152 mg %) and lower levels in the brain (51 mg %), liver (51.4 mg %), spleen (45 mg %) and the kidney (36 mg %) (Table 43) Shugaev also exposed rats to butadiene at $285,000 \text{ mg/m}^3$ for 1 hour. When determinations were made 0.1 min. after exposure was terminated, levels were about 34 mg % in brain and liver tissue; however, no butadiene (or only a trace) was found in these tissues 90 minutes after exposure (Table 44). Shugaev (1969) reported a correlation between butadiene concentration in the brain and narcotic state. Rats inhaling butadiene (and other hydrocarbons tested) were in a state of deep narcosis after 1 hour's exposure. When exposure was terminated, movement appeared within 4-5 minutes and muscular control was normal after 60 minutes.

Levels of butadiene were also determined in several parts of the nervous system and in the liver of cats. Two cats were exposed at a level such that death occurred within one hour (this level was not reported). The highest concentration of butadiene was found in the spinal cord and pons (Table 45).

3) Metabolism

The urine of rabbits inhaling, daily, atmospheres containing 20-25% ($442,000-552,500 \text{ mg/m}^3$) butadiene in subacute and chronic experiments (see Sections III B-1-a) was analyzed for formic acid, oxalic acid, aldehydes, and materials oxidizable by periodic acid (1,2-glycols, glyoxal, glycollic aldehyde, pyruvic aldehyde, acetoin, biacetyl and erythritol) as possible butadiene metabolites. No "appreciable differences" were found between the urine of exposed and control rabbits for these compounds; no data are presented to support this (Carpenter et al., 1944).

Table 43
Distribution of Butadiene^a After Exposure to
LC₅₀ (Shugaev, 1969)

<u>Organ</u>	<u>Average Butadiene Levels, mg% (95% Confidence Limit)</u>	
	<u>Rat^b</u>	<u>Mouse^c</u>
Brain	50.8 (43.3-58.3)	54.4 (39.9-69.0)
Liver	51.4 (45.3-57.5)	-d
Kidney	36.3 (29.2-43.4)	-d
Spleen	45.0 (39.7-50.3)	-d
Perinephric Fat	152.1 (120.6-183.7)	-d

^a precise time of determination not given

^b exposure to 285,000 mg/m³ for 2 hr (LC₅₀); data from 7 or 10 trials

^c exposure to 270,000 mg/m³ for 4 hr (LC₅₀); data from 10 trials

^d not determined

Table 44
Distribution of Butadiene in the Brain and Liver
of Rats at Several Time Intervals after Acute
Exposure^a (Shugaev, 1969)

<u>Time after Removal from Chamber (1 min.)</u>	<u>Average Concentration, mg% (95% Confidence Limit)</u>	
	<u>Brain</u>	<u>Liver</u>
0.1	34.6 (24.1-42.3)	33.8 (27.6-39.2)
15	6.7 (7.1-12.3)	10.9 (6.2-15.7)
30	4.3 (3.1-5.3)	5.9 (3.4-7.6)
60	2.9 (1.8-4.2)	3.3 (2.7-4.2)
90	0 - traces	0 - traces

^a exposure to 285,000 mg/m³ for 1 hour
(LC₅₀ 4 hour = 285,000 mg/m³)

Table 45
Distribution of Butadiene in the Central Nervous
System and Liver of Acutely Intoxicated Cats
(Shugaev, 1969)

Tissue	Butadiene Concentration (mg%)	
	Cat No. 1	Cat No. 2
Cortex cerebri in region Gyrus centralis anterior	32	24
Substantia alba in region Capsula interna	42	33
Cortex cerebelli	34	22
Medulla oblongata	45	44
Mesencephalon in region corpora quadrigemina	36	42
Pons Varolii	67	50
Spinal cord jugular section	70	59
Liver	31	28

^a neither dosage nor precise time of tissue measurement were reported; exposure set so cats died during 1 hr. exposure

b. Cyclooctadiene

The metabolism of 1,5-cyclooctadiene was studied in 6 doe rabbits (2.5-3 kg) and 6 female rats (200-250 g) (Waring, 1971). Oral doses of 1.5 m mol/kg (162 mg/kg) of 1,5-cyclooctadiene were administered by gavage. Twenty-four hour samples were collected and analyzed by gas liquid chromatography and mass spectrometry. Metabolites identified in the urine are given in Table 46 and include the glucuronide and sulfate conjugates, and 2 unidentified mercapturic acids (perhaps methyl esters of diacetoxycyclo-octyl mercapturic acids). In a separate experiment, Waring (1971) showed that the liver is the major source of sulfur for conjugation to form mercapturic acids. Rats previously dosed with ³⁵S were fed 1,5-cyclooctadiene, and then killed 2 hours later. The liver was the only tissue in which the content of ³⁵S decreased significantly. This is in agreement with observed decreases in liver glutathione (GSH). Female rats (200-250 g) were fed 1.5 m mole/kg of 1,5-cyclooctadiene. Total liver glutathione was reduced to 66% of control values after 2 hours and 73% after 3 hours.

Table 46
Excretion of Conjugates in Urine of Rats and Rabbits
After Oral Dosing with 1,5-Cyclooctadiene^a
(Waring, 1971)

Conjugates in Urine ^b	% Dose (range)	
	Rabbit (N=6)	Rat (N=6)
Glucuronide	53.5 (48.4-58.2)	- ^c
Ethereal Sulfate	22.8 (18.1-24.6)	- ^c
Mercapturic Acids		
A	5.4 (4.3-6.2)	5.5 (4.6-6.6)
B	16.3 (14.8-17.7)	18.9 (13.4-21.3)

^a 1.5 m mole/kg (162 mg/kg)

^b 24-hr urine

^c no determinations made

C. Other Animals

No data are available on the toxicity of butadiene or its oligomers to species other than humans or laboratory mammals. Several authors have erroneously cited data from Garrett (1957) on fish toxicity. Garrett's paper, however, mentions 1-cyano-1,3-butadiene and not 1,3-butadiene.

D. Plants

Several authors have investigated the toxicity to plants of butadiene monomer and butadiene in the presence of atmospheric constituents (e.g., nitrogen oxide, ozone). While the monomer itself had little effect on the species tested, products forming in the presence of butadiene may be harmful, as discussed below.

Haagen-Smit et al. (1952) tested several constituents of smog, including butadiene, for toxic effects on five crop plants under controlled laboratory

conditions. A mixture of 5 ppm butadiene and 0.15 ppm ozone was used to fumigate the plants over five hours. Leaf damage was compared to known smog damage. "Typical" smog damage was considered to be: i) metallic sheen, silvering, or bronzing on spinach, endive, and beets; ii) speckled necrosis on oats and alfalfa; and iii) marginal bleaching on alfalfa. Atypical damage was often characterized by wilting, necrotic areas, tip burning, chlorosis, bleaching or pitting. In the experiment described above, typical smog damage occurred to the leaves of endives; typical, but not severe damage occurred to spinach oats and alfalfa. Beet leaves were damaged, but not in a manner typical of smog damage (Table 47).

In a second series of experiments, mixtures of butadiene and oxides of nitrogen were used to fumigate the indicator plants for 1.5-5 hours (Table 48). No damage occurred after exposure to mixtures of 2.0 ppm butadiene - 2.5 ppm N_2O_3 or 0.5 ppm butadiene - 4.5 ppm NO_2 . However, higher concentrations of the latter components (5 ppm butadiene - 7.0 NO_2) caused typical smog damage to spinach and endive leaves and typical nonsevere leaf damage to beets. Atypical injury to oats and alfalfa occurred.

Altschuller et al. (1966) subjected 3 species of plants to the irradiation products formed during the first four hours of photooxidation of 3.30 ppm butadiene and 0.85 ppm nitrogen oxides. The primary reaction products were formaldehyde, acrolein, aliphatic aldehydes, and ethylene (0.85, 1.0, 1.15, and 0.002 ppm by volume, respectively); trace amounts of peroxyacetyl nitrate (PAN) also formed. There was no leaf damage to individuals of the tobacco wrapper (Nicotiana tabacum), petunia (Petunia hybrida), or young pinto beans (Phaseolus vulgaris). The authors account for the absence of plant damage to young pinto beans by the formation of only trace amounts of PAN, a compound to which these species are particularly sensitive.

Table 47
Effect of Butadiene and Either Ozone or Oxides of
Nitrogen on Plants (Haagen-Smit et al., 1952)

<u>Conditions</u>	<u>Results</u>			
Mixture of (ppm, vol/vol)				
Butadiene	2.6	5.0	0.5	2.0
Ozone	0.15	-	-	-
NO ₂	-	7	4.5	-
NO ₃	-	-	-	2.5
Exposure (hours)	5	1.5	4.5	5
Injury to leaves ^a				
Spinach	t	T	0	0
Endive	T	T	0	0
Beets	A	t	0	0
Oats	t	A	0	0
Alfalfa	t	A	0	0

^a injury scored as follows (refer to text):

T = typical smog damage

t = typical smog damage but not as severe

A = damage not typical of smog damage

0 = no injury

Tests have also been conducted on the butadiene monomer alone. Heck and Pires (1962) tested 14 low molecular weight hydrocarbons, including butadiene, for effects on plant growth and development. Fumigation at 1,000 ppm (2,210 mg/kg) butadiene for 7 days produced only slight injury in cotton, cowpea, and tomato; no injury was reported for coleus, sorghum, or soybean. In further tests with butadiene, no easily recognizable injury occurred after a three week fumigation at 10 ppm (22.1 mg/m³) (for coleus, cotton, and tomato) or at 100 ppm (221 mg/m³) butadiene (for cotton and tomato). The nature or frequency of the injuries were not specifically stated. Heck and Pires (1962) summarized the tests by stating that butadiene resulted in 0% injury at 10 ppm and <5% injury at both 100 and 1,000 ppm.

Butadiene was one of about 35 compounds tested for biological activity and compared to the action of ethylene in pea seedlings (Pisum sativum) (Burg and Burg, 1967). In the Straight Growth Test, ethylene-treated peas first swell then elongate 50% less than controls, described by Michaelis-Menton kinetics. In this test, the concentration of ethylene required for half-maximum activity is 0.1 ppm; for butadiene, 500,000 ppm (1,105,000 mg/m³) was required but this activity may be due to the contamination of the butadiene with 0.2 ppm ethylene.

Abeles and Gahagan (1968) also compared various compounds, including butadiene, to the action of ethylene. The role of 7 compounds in accelerating petiole abscission was tested in the red kidney bean Phaseolus vulgaris. Half maximum stimulation of abscission occurred at about 0.1 ppm ethylene but at > 10,000 ppm butadiene; butadiene and 1-butene were the least active of the compounds tested. The percent abscission over controls after 4 hours exposure depended on the concentration tested, as shown below for butadiene:

<u>Butadiene Conc. (ppm)</u>	<u>% Abscission over Controls</u>
1	0
10	2
100	5
1,000	8
10,000	18

IV. SPECIAL EFFECTS

A. Mutagenicity

1. Butadiene

De Meester et al. (1978) determined butadiene and its possible metabolite, butadiene monoxide, to be weakly mutagenic in several test strains sensitive to base-pair substitution mutagens. The study was prompted by the structural similarity between butadiene and other monomers known to be mutagenic (e.g., vinylidene chloride, 2-chlorobutadiene, styrene, acrylonitrile); these monomers all contain vinylic groups.

The procedure involved adding Salmonella typhimurium (strains TA 1530, TA 1535, TA 1537, TA 1538, TA 98, and TA 100) to the test chemical, pouring the mixture onto agar plates and counting the number of revertants to histidine prototrophy (his+) per plate after a period of incubation. Tests were performed both in the absence and presence of a metabolic activation system, fortified S-9 fractions of rat liver homogenate. The results for butadiene appear in Table 48. Strains TA 1530 and TA 1535 showed a direct (in absence of S-9 fraction) and an indirect (in presence of S-9 fraction) mutagenic response to butadiene. When the S-9 fraction was used, more revertants occurred at the lower of 2 S-9 concentrations tested, possibly due to an inadequate composition of S-9 mix. The other strains showed no mutagenic response either with or without metabolic the activation.

The number of revertrants was determined over time (0-72 hours) for strain TA 1530. During the first hours, the reversion rate was low but increased to a maximum after about 24 hours; however, the percentage of butadiene in the atmosphere had decreased by about 25% during this period. This phenomenon

Table 48
Mutagenic Effect of Butadiene on Strains of S. typhimurium in the
Presence and Absence of a Fortified S-9 Fraction
(De Meester et al., 1978)

	No. of his ⁺ Revertants/Plate					
	TA 1530	TA 1535	TA 1537	TA 1538	TA 98	TA100
Controls						
Without S-9 fraction	13	14	7	25	29	158
With S-9 fraction ^a	13	14	20	24	35	146
Butadiene ^b						
Without S-9 fraction	80	52	11	28	15	118
With S-9 fraction ^b	43	37	10	34	34	98
Butadiene ^b						
Without S-9 fraction	58	55	15	31	14	108
With S-9 fraction ^c	65	65	13	23	28	154

^a300μl S-9/ml mix used; total incubation time was 72 hours

^bincubation time in dessicator 20 hours; at that time percentage of butadiene in dessicator atmosphere was ~70%

^c200μl S-9/ml mix used; total incubation time 44 hours

might be related to the low solubility of butadiene in the aqueous phase. The authors also carried out mutagenicity tests using the usual Ames standard plate method (mixed substrate in top agar) and there was no increase in the number of revertants compared to controls; no data were presented on this, however.

For butadiene monoxide there was no mutagenic response in TA 1537, TA 1538 or TA 98 strains at the concentrations tested of (1-250 μmoles/plate). For strains TA 1530, TA 1535 and TA 100 reversion to histidine prototrophy occurred without metabolic activation within a range of 60 to 100 μmoles/plate. For strain 100, the reversion rate at 100 μmoles plate was twice

that of the spontaneous rate. For strains TA 1530 and TA 1535, the mutation rate was 10 times the spontaneous reversion rate at 100 μ moles/plate; butadiene concentrations higher than this were toxic.

Strains TA 1530 and TA 1535 are sensitive to base-pair substitution mutagens, suggesting that for both butadiene and butadiene monoxide, base-pair substitutions in the bacterial DNA are involved. Furthermore, since both strains were sensitive to the same strains the authors suggest that butadiene monoxide may be a primary metabolite of butadiene.

2. Possible Metabolites

As discussed above, de Meester et al. (1978) suggest that butadiene monoxide is a possible oxidative metabolite of butadiene. They showed that butadiene monoxide induces reversion to histidine prototrophy in several strains of Salmonella typhimurium. These researchers also postulated that diepoxybutane might be another oxidative metabolite of butadiene.

Diepoxybutane was mutagenic in several test systems, as shown below (reviewed in IARC, 1976b):

- induced reverse mutations in strain TA 1535 of S. typhimurium, in Schizosaccharomyces pombe and in E. coli.
- induced reverse mutations in adenine-requiring mutant 38701 of Neurospora crassa
- produced mitotic gene conversions in strain D4 of Saccharomyces cerevisiae
- produced sex-linked recessive lethal mutations, visible mutations, semi-lethal mutations, translocations and minute mutations in Drosophila melanogaster.

B. Carcinogenicity

1. Butadiene

Butadiene was scheduled to be tested by the National Cancer Institute for carcinogenicity. However, the contract to the performing organization was terminated and there are no projected dates to begin testing again (Chase, pers. comm., 1978).

2. Possible Metabolites

De Meester et al. (1978) speculated that butadiene monoxide (1,2-epoxybutene-3) and diepoxybutane might be oxidative metabolites of 1,3-butadiene. This suggestion was based primarily on structural similarities between butadiene and other monomers (i.e., vinylchloride and styrene), which form reactive epoxide intermediates. Butadiene monoxide and racemic forms of diepoxybutane have been reported to possess carcinogenic properties when applied to the skin of mice (Van Duuren et al., 1963). The data and experimental method appear in Table 49. In addition, subcutaneous injection of d,l-1,2:3,4-diepoxybutane (0.1 or 1.1 mg in tricaprylin) in female mice once a week for a year resulted in the development of local fibrosarcomas (5/50 and 5/30 mice for 0.1 and 1.1 mg groups, respectively). Solvent controls developed no local sarcomas. Female Sprague-Dawley rats given 1 mg i.p. d,l-1,2:3,4-diepoxybutane in tricaprylin once a week also developed local fibrosarcomas (9/50 animals) (Van Duuren et al., 1966).

3. Oligomers

The carcinogenic potential of vinylcyclohexene and its hydroperoxide were evaluated in male Swiss-Millerton mice (Van Duuren et al., 1963). Commercial vinylcyclohexene was purified to remove oxidation products by distillation. The hydroperoxide was prepared as a 0.5% solution of VCH. Application of both compounds in benzene to the skin of mice 3 times per week for life resulted in

Table 49

Carcinogenicity of Butadiene Monoxide and Diepoxybutane in Male Swiss-Hillerton Mice (Van Duuren et al., 1963)^a

Concentration	Butadiene Monoxide	dl-1,2;3,4-Diepoxybutane	meso-1,2;3,4-Diepoxybutane	Acetone (control)	No Treatment (control)
Solvent	-	10% acetone	10% acetone	-	-
No. tested	30	30	30	90	207
Median survival time (days)	237	78	154	134-330	112-624
Tumor incidence ^b	3	2	6	8	13
% of Total	10%	6.7%	20%	8.9%	6.3%
Cancer incidence ^c	1	1	4	0	1
% of Total	3.3%	3.3%	13.3%	0%	0.5%

^aCompounds applied to skin 3 times per wk for life, 100 mg/painting

^bRefers to benign papillomas and squamous cell cancers

^cRefers to squamous cell cancers

extensive skin damage. The experimental conditions appear in Table 50. Tumor frequencies for 150 benzene (control for solvent) and 207 no-treatment controls were 7.3 and 6.3%, respectively; one animal in each group developed a cancer. Of 30 mice tested with vinylcyclohexene, 6 (20%) developed skin tumors; 1 of these tumors was a squamous cell cancer. The incidence for the hydroperoxide was higher; thirteen of 36 mice (34%) developed tumors, 5 of which were cancerous. The authors suggest the possibility that the VCH contained a small amount of the hydroperoxide formed by autooxidation.

In another experiment using "oxygen-free" VCH (precluding oxidation), 0.1 ml VCH (in a 10% solution in benzene) was applied to the skin of 30 Swiss-Millerton mice 3 times/week for life. No carcinogenic effect was observed (Van Duuren, 1965).

The International Agency for Research on Cancer (IARC, 1976a) examined the two studies by Van Duren and concluded that the data do not allow an evaluation of carcinogenic risk as the testing was only by skin application.

Table 50
Carcinogenicity Testing of Vinylcyclohexene (VCH) and
the Hydroperoxide of VCH in Male Swiss-Millerton
Mice (Van Duuren et al., 1963)

	VCH ^a	1-Hydroperoxy-4-Vinylcyclohexene ^b	Benzene ^b	No Treatment
Concentration	50%	0.5%	(control)	(control)
Solvent	benzene	1:1 benzene:VCH	-	-
No. tested	30	38	150	207 ^c
Median survival time (days)	375	165-403	262-412	112-624
Tumor incidence ^c				
Number	6	13	11	13
% of total	20%	34%	7.3%	6.3%
Cancer incidence ^e				
Number of mice	1	5	1	1
% of total	3.3%	13%	0.7%	0.5%

^a applied to skin 3 times/week for life; 45 mg/painting

^b applied to skin 3 times/week for life; 100 mg/painting

^c not including 60 female GAF mice

^d tumor incidence refers to benign papillomas and squamous cell cancers

^e cancer incidence refers to squamous cell cancers

V. REGULATIONS AND STANDARDS

A. Federal Regulations

1. Occupational Safety and Health Administration

The occupational exposure to butadiene is limited by the Occupational Safety and Health Administration (OSHA, 1970) to an 8-hour time-weighted average of 1,000 ppm (2,200 mg/m³) (Table Z-1; 29 CFR 1910.1000). This is the same value recommended by the American Conference of Governmental Industrial Hygienists (ACGIH, 1977; see Section V-D).

2. Department of Transportation

Butadiene offered for transport must be inhibited against polymerization. Regulations pertaining to the transport of inhibited butadiene are contained in the Hazardous Materials Table promulgated under the Hazardous Materials Transportation Act (1975; 49 CFR 172.101; PL 93-633). Butadiene is classified as a flammable gas. Requirements for the charging and shipping of compressed gases are detailed in 49 CFR 173.304 and 173.314-5. A motor vehicle or rail car transporting butadiene must be placarded on each side and each end with a red placard identifying the shipment as a flammable gas.

Inhibited butadiene cannot be shipped by a passenger-carrying railcar or aircraft. When shipped by cargo-only aircraft, a maximum of 300 pounds may be contained in each package shipped. For cargo vessels, butadiene may be stowed "on deck" or "under deck", away from living quarters.

3. Environmental Protection Agency

Effluent limitation guidelines exist for discharges associated with butadiene manufactured by any process, which includes the oxidative dehydrogenation of butene (40 CFR 414). Butadiene is the only organic chemical whose process wastewater is regulated as a point source. Three levels of control

technology for butadiene manufacture are outlined in title 40 of the code of Federal Regulations and appear in Table 51. The first is for the best practicable control technology currently available (BPCTCA). The second is for the best available technology economically achievable (BATEA). Finally, effluent limitations exist for new sources.

4. Food and Drug Administration

Butadiene is considered an indirect food additive by the Food and Drug Administration under 21 CFR parts 174ff. Food contact use is regulated for butadiene-containing polymers and copolymers, including use in the following: adhesives; polymeric coatings; paper and paperboard components; single and repeated use food contact surfaces; and cellophane.

B. State Regulations

Agencies in 15 selected states, including those containing production and major end-use sites, were contacted about state-level regulations. Their response appear in Tables 52-54.

1. Workplace Standards

Those states responding to information requested on workplace standards indicated that they enforce the standards set by the Occupational Safety and Health Administration (Table 52).

2. Food Contact

States responding indicated reliance on the regulations of the U.S.D.A. and F.D.A. (Table 52).

3. Water Quality

Butadiene is indirectly limited by general water quality standards in many states (Table 53).

Table 51
Effluent Limitations for the Manufacture of Butadiene by
Oxidative Dehydrogenation (40 CFR 414)

Effluent Characteristic ^a	Effluent Limitations ^b	
	Maximum for Any 1 Day	Average of Daily Values for 30 consecutive days shall not exceed:
A. Best Practicable Control Technology Currently Available		
BOD ₅	2.3	1.0
TSS	2.3	1.0
pH	6.0-9.0	6.0-9.0
B. Best Available Technology Economically Achievable		
COD	7.8	4.2
BOD ₅	0.57	0.27
TSS	0.94	0.50
pH	6.0-9.0	6.0-9.0
C. New Source Standards		
COD	7.8	4.2
BOD ₅	0.57	0.27
TSS	0.94	0.50
pH	6.0-9.0	6.0-9.0

^a BOD = biological oxygen demand at 5 days

COD = chemical oxygen demand

TSS = total suspended solids

^b units = pounds per 1,000 lb product

Table 52
Regulations for Butadiene Food Contact and Workplace Standards in
Selected States in Response to Queries

	Food Contact	Workplace Standards
California	*	*
Connecticut	*	*
Delaware	*	*
Kentucky	-	-
Louisiana	-	-
Missouri	-	-
New Jersey	*	*
New York	*	-
Ohio	-	-
Pennsylvania	-	*
South Carolina	*	*
Tennessee	-	*
Texas	-	-

*Federal standards followed; dashes indicate no response

Table 53
Water Standards for Butadiene in Selected States in
Response to Queries

State	Standard
California	no response
Connecticut	no specific water quality standards or regulations; subject to case-by-case technical permit review by Water Compliance and Hazardous Substance Unit
Delaware	not specifically controlled
Kentucky	no response
Louisiana	case-by-case permit review for discharges
Missouri	general water quality standards apply
New Jersey	comply with federal discharge requirements under FWPCA
New York	no water quality standards for BD
Ohio	general water quality standards apply; State Law: OAC-3745-1
Pennsylvania	general water quality standards apply
South Carolina	indirectly limited by general water quality criteria
Tennessee	general standards for toxic substances and organics apply
Texas	measured indirectly as BOD ₅ or COD in individual discharge permits issued to manufacturers.

Table 54
Air Standards for Butadiene in Selected States in
Response to Queries

State	Standard
California	control as "reactive organics" in California basins in which federal oxidant standards is exceeded
Connecticut	emissions restricted to 8 lb/hr., 40 lbs/day for organic solvents; State Law: Section 19-508-20f(2)
Delaware	general air quality standards apply; State Law: Reg. 1-XXIII of Dept. Nat. Res. & Env. Control (for air pollution)
Kentucky	no response
Louisiana	regulations for storage of relative organic carbons may apply
Missouri	no specific regulations
New Jersey	general restrictions for volatile organic substances and ambient air quality standards apply; State Law: NJEPA N.J. Adm. Code Title 7, Chp. 27
New York	processes, exhaust and/or ventilation systems are regulated under State Law: Industrial Process Air Pollution Control Rule, part 212
Ohio	considered photochemically reactive (PR) by the Ohio Environmental Protection Agency assuming BD in liquid state with another organic material. Emission requirements for PR materials is 8 lbs/hour and 40 lbs/day per equipment, machine or article. However, if the source has a control device (that is at least 85% efficient) the mass emission requirement is waived for liquid organic materials conducted by flame, heat-cured or heat-polymerized emission is 3 lbs/hr and 15 lbs/machine; State Law: OAC 3745-21-01(C)
Pennsylvania	no weight rate emission limitations for BD; standards for organic compounds apply for storage and loading; State Law: Pa. Air Pollution Control Act
South Carolina	no specific regulations
Tennessee	general process emission standards; State Law: 1200-3-7-.07
Texas	State Law: Reg. 7 rule 505.2 specifically lists regulations for BD emissions. Waste stream must be burned at temperature > 1300°F in a smokeless flare or a direct flame incinerator before it may enter the atmosphere. Regulations provided for storage of volatile carbon compounds.

4. Air Emissions

Butadiene emissions are regulated either directly or indirectly in several states (Table 54). In Ohio, butadiene is considered photochemically reactive and by definition, emissions are limited to 8 lbs/hour and 40 lbs/day per equipment, machine, or article. However, if the source has a control device that is 85% efficient this emission requirement is waived. For liquid organic materials which are contacted by flame, or are heat-cured or heat-polymerized, emission is limited to 3 lbs/hour and 15 lbs/machine. In Texas, butadiene waste streams must be burned at temperatures greater than 1300°F in a smokeless flare or a direct flame incinerator before it may enter the atmosphere. In many other states, general air quality or emission standards apply.

C. Foreign Countries

Agencies in several countries were contacted about butadiene regulations. In addition, specific laws and regulations were consulted.

1. United Kingdom

The work place standards in the U.K. for butadiene are the following:

TLV (threshold unit value) = 1,000 ppm (2,200 mg/m³)

STEL (short term exposure limit) = 1,250 ppm (2,750 mg/m³)

In general, the U.K. uses exposure units drawn up by the ACGIH (American Conference of Governmental Industrial Hygienists).

Air pollution control for industrial processes is under control of HM Alkali and Clean Air Inspectorate in England and Wales; in Scotland, HM Industrial Pollution Inspectorate under authority of the following: The Alkali Act, (6 Edw.7.C.14); the Health and Safety at Work Etc. Act 1974 (1974 Chapter 37); and, the Control of Pollution Act 1974 (1974 Chapter 40). Control of butadiene might be effected under these acts, but there are no specific air

standards for butadiene. Similarly, while there are no specific water quality standards for butadiene, control could be accomplished under The Water Act of 1973, among other acts.

2. West Germany

The maximum allowable workplace concentration (MAK) of butadiene is 1000 ppm (2200 mg/m^3) (BNA:MAK, 1977); it is the same in East Germany.

Air emission standards for butadiene and other compounds are contained in the Air Purity Regulations (6MBI 1974). In waste gas, butadiene cannot exceed 150 mg/m^3 (when flow rate is 3 kg/hr or more).

There are no specific water quality standards for butadiene.

3. Japan

Butadiene is not listed as a toxic substance under the Air Pollution Control Law (Law No. 97 of 1968).

The Water Pollution Control Law (Law No. 138 of 1970) sets forth regulations for synthetic rubber manufacturing and other industries in which butadiene is used; however, emission of butadiene monomer does not appear to be controlled.

4. Canada

Occupational health falls under provincial rather than federal jurisdiction. In general, provincial standards reflect ACGIH and/or OSHA recommendations.

The Environmental Protection Service (EPS) in Canada is developing regulations and guidelines to reduce air and water pollution. Effluent guidelines are currently being drawn up for the organic chemicals industry (Anon., 1978d) which might possibly regulate butadiene.

No tolerances have been set for butadiene migration from food-contact polymers.

5. Others

Occupational exposure limits in other countries not discussed above are as follows (Scala, 1977):

	<u>ppm</u>	<u>mg/m³</u>
USSR	45	100
Bulgaria	45	100
Czechoslovakia	230	500
Finland	1000	2200
Poland	45	100
Rumania	682	1500
Yugoslavia	1000	2200

D. Other Standards

In 1971 the American Conference of Governmental Industrial Hygienists (AICGH, 1971) recommended a threshold limit value (TLV) of 1,000 ppm (2200 mg/m³) for butadiene based primarily on the low toxicity reported in animals by Carpenter et al., (1944, see section III). This TLV appears "to offer a comfortable margin of safety from effects of exposure". In 1977, the AICGH recommended that the Short Term Exposure Limit (STEL) maximum for butadiene be 1,250 ppm (2,750 mg/m³).

E. Current Handling Practices

1. Handling, Storage, and Transport

A manual published by the Manufacturing Chemists Association give the procedure for the safe handling and transport of butadiene, which is described as a dangerous fire hazard when exposed to heat, flame or strong oxidizers (MCA, 1974). Commercial liquified butadiene is inhibited against peroxide formation and polymerization, but uninhibited butadinene presents problems of heat and pressure development at elevated temperatures, as in fire conditions. Butadiene vapors are uninhibited and "popcorn" polymers may form

by auto-addition, plugging pipelines or storage tank vents. A problem is the handling of butadiene is the formation of butadiene dimer, particularly at elevated temperatures; no inhibitor for this reaction is known. Because of this problem, commercial butadiene is usually stored under conditions of refrigeration rather than under pressure. Also, refrigerated storage is usually more economical than pressure storage (Exxon, 1974). The liquified gas is cooled by auto-refrigeration and stored at a temperature yielding vapor pressure of 1-10 psig; the vapor is then cooled and condensed. Pressure storage is used only to store small quantities of butadiene in cylinders and sample bombs (Exxon, 1974). These should be stored in an outdoor, detached place or a well-ventilated cool place. Cylinders should be stored vertically (not-stacked) and protected against physical damage (ITII, 1975).

Butadiene is usually shipped in steel cylinders (100 lb. capacity), tank cars or tank trucks. Cylinders are shipped by motor freight, rail freight or railway express (Exxon, 1974).

2. Personnel Exposure

The Manufacturing Chemists Association (1974) suggested that air-supplied masks be used during exposures to high concentrations (20-25%) of butadiene vapors. Other protective equipment which should be made available for use in case of spills or equipment failure includes goggles, aprons or suits, boots, emergency deluge showers, and eye wash fountains.

In the case of overexposure to butadiene vapors the victim should be removed to fresh air; oxygen resuscitation may be necessary (MCA, 1974). In the case of skin contact with liquid butadiene, the affected area should be placed in water at 37.5°C until circulation resumes. (Exxon, 1977).

3. Accident Procedures

In the event of spills, all ignition sources should be eliminated. Petro-Tex (n.d.) suggested covering spills with a foam blanket with water fog. Leaks should be covered with water fog or a steam blanket. Spills should be prevented from entering sewers or low areas. Small quantities of spilled butadiene should be vented to the atmosphere or to an open space with adequate ventilation, whereas "appreciable quantities" should be burned or flared (Exxon, 1977; Petro-Tex, n.d.).

VI. EXPOSURE AND EFFECTS POTENTIAL

A. Butadiene

Environmental exposure to butadiene may occur from several sources: 1) production 2) end-use; 3) storage; and 4) transport. Also, butadiene is a minor component of hydrocarbons in urban air. For humans, it appears that the highest exposure potential is in the workplace. Levels up to 1,000 ppm (2200 mg/m³) are allowable in the workroom, as an 8-hour time-weighted average. This value is based primarily on the low toxicity of butadiene to laboratory animals (see Section III-B). Although acute over-exposures may occur through improper handling and accidents, there have been no reports in the U.S. or Western European literature of any chronic effects arising from industrial use of butadiene. Another consideration of occupational exposure is the extreme flammability and reactivity of butadiene. For example, the Manufacturing Chemists Association (MCA, 1966) described an industrial accident involving a ruptured pipeline which released butadiene vapors. The vapors were ignited by a gas-engine driven compressor and an employee standing 40 feet from the tank at the time of ignition received extensive burns. The leak occurred when a plug of butadiene "popcorn" polymer ruptured the pipeline; "popcorn" growth is usually associated with the presence of oxygen.

As mentioned above, exposure may also be possible during several phases of production and use. Because only limited monitoring data are available, it is difficult to adequately assess this potential. These monitoring data, discussed in detail in section II, indicate that the butadiene monomer is only a minor constituent of emissions from production facilities. In the production of SBR, small amounts of butadiene enter the atmosphere from the butadiene absorber vent and as fugitive emissions (Table 23) (Pervier et al., 1974a).

In a study of atmospheric emissions from an adiponitrile production facility, butadiene comprised 3.8% of the total amount of hydrocarbons emitted (Pervier et al., 1974b). Butadiene has been identified in the wastewater of rubber manufacturing plants by Day (1975), and low levels of butadiene have been identified in urban air (<10 ppb) and gasoline (<1 ppb) (see Section II-C-5).

Another source of butadiene is from monomer storage facilities. One study reported that .00017 lb were emitted per lb of SBR produced during tank farm storage (Pervier et al., 1974a).

The possibility also exists for environmental contamination during transportation accidents or tank car failure. Butadiene, a gas at ambient, temperature, is usually shipped under pressure as a liquid. Release of butadiene from a pressurized tank failure, for example, will result in flash vaporization of the liquid and the formation of an aerosol. Slater (1978), in reviewing the formation and hazards of vapor clouds, found that the dispersion of vapor clouds depends on factors such as micrometeorology, temperature, topography, thermodynamic properties and aerodynamic effects. Smaller leaks are less likely to ignite, because the concentration may fall below the lower flammable limit before ignition occurs (2% for butadiene). For larger clouds, ignition is more likely. Slater (1978) listed an accident involving a vapor cloud of butadiene in Holland during 1971; 8 people were killed and 21 were injured. He also mentioned 2 explosion accidents involving light hydrocarbons: i) Perris, Netherlands, 1968 in which 2 people were killed and 75 injured; the blast shattered windows 1 mile away and ii) Puerto la Cruz, 1969 in which 5 people were killed; there was extensive glass and ceiling damage in the town.

Butadiene present in the atmosphere from any source (i.e., leaks, production emission) will not persist. Butadiene is highly reactive. It participates in atmospheric photolysis reactions, and also reacts with nitrogen oxides and ozone found in the atmosphere. In a laboratory study, Stephens and Burleson (1967) showed that butadiene in air samples will disappear after 4 hours of irradiation with U.V. light. However, samples kept in the dark still contain butadiene after 24 hours (Table 29). Under atmospheric conditions, the presence of nitrogen oxides and ozone, as well as light, is critical to removal.

Another approach to assess environmental exposure is one taken by Fuller et al., (1976). Using a scoring system based on production, volatility and toxicity, they examined the potential of 637 organic chemicals, including butadiene, to enter the atmosphere from industrial sources and pose a toxicological threat. For butadiene, a final score of 3 was assigned taking into account factors of production, properties and toxicity. A maximum score of 125 was possible. The scoring system appears to be most useful when comparing chemicals. Scores for several are: acrylamide, 4; acrylonitrile, 20; ethylene, 9; ethylene glycol, 11; and propylene, 4.

Only low-level environmental contamination of butadiene may be expected, except during a spill situation. The potential hazards from low-level contamination do not appear to be high. Butadiene is volatile and reactive, thus subject to chemical degradation. A short residence time is expected.

b. Oligomers

Vinylcyclohexene is a contaminant in all butadiene samples, but its formation is temperature-dependent. When butadiene vaporizes, as in the tank failure discussed above, vinylcyclohexene, being less volatile will remain longer

at the spill site. The persistence of this compound under environmental conditions has not been investigated.

Butadiene oligomers have been identified in the workroom. Rappaport and Fraser (1977) detected low levels of vinylcyclohexene (0.313 and 0.408 mg/m³ in 2 areas), 1,5-cyclooctadiene (0.0277 and 0.0285 mg/m³) and 1,5,9-cyclodecatriene (0.0481 and 0.1054 mg/m³) in a passenger tire curing room. These oligomers probably originated from cis-polybutadiene rubber used in tire manufacture. No other data are available on environmental contamination by butadiene oligomers.

TECHNICAL SUMMARY

1,3-Butadiene is a basic monomer used to produce styrene-butadiene rubber (53%), polybutadiene rubber (18%), neoprene (7%), nitrile rubber (3%), adiponitrile (8%), acrylonitrile-butadiene-styrene resins (6%), as well as other products (5%) (Anon., 1977a). About 3.2 billion pounds of rubber-grade butadiene were produced during 1977 (U.S. Int. Tariff Comm., 1977) by three commercial processes (dehydrogenation of n-butane or n-butene, or coproduct of ethylene manufacture) and by about 15 manufacturers at more than 20 locations. These locations are in Texas (70%), Louisiana (20%), and Puerto Rico (10%). Total capacity is about 4.9 billion pounds.

Butadiene reacts with itself to form cyclic oligomers. Examples of commercially important oligomers are 4-vinylcyclohexene, 1,5,9-cyclododecatriene and 1,5-cyclooctadiene. Cyclododecatriene is used primarily as a precursor to nylon with DuPont being the only current domestic producer. Cyclooctadiene is used in ethylene-propylene terpolymer production and is available from Cities Service Co. Vinylcyclohexene is an impurity in butadiene formed by dimerization; patents have described potential applications for insecticides, plasticizers and as an intermediate in preparing aliphatic hydrocarbons and antioxidants. Vinylcyclohexene is obtained as a byproduct of butadiene manufacture and not produced directly.

Limited monitoring data indicate that low levels of butadiene can enter the environment during production, end-use, storage and transport. Accidental spills and leaks appear to be the greatest potential for environmental exposure. Butadiene has been identified as a constituent of urban air (<10 ppb or 0.02 mg/m³) (Table 26) and gasoline (<1 ppb, Stevens and Burleson, 1967). Butadiene oligomers were identified in the workplace of a tire vul-

canization area (Rappaport and Fraser, 1977) but the extent of environmental contamination is unknown.

Butadiene is a gas at ambient temperature and pressure. When released into the environment, butadiene will vaporize rapidly. In addition to being volatile, butadiene is highly reactive chemically and will not persist in the environment. Butadiene participates in atmospheric photolysis reactions, and will react with nitric oxide, forming acrolein, aliphatic aldehydes, ethylene, formaldehyde, and peroxyacetyl nitrate (Altshuller et al., 1966; Heuss and Glasson, 1967). These reaction products of butadiene and nitrogen oxides resulted in eye irritation to humans (Altshuller, 1966; Heuss and Glasson, 1967). Butadiene also reacts with ozone (Hanst et al., 1959).

Analytical methods exist for determining butadiene in several media. Most employ gas chromatography.

For humans, butadiene vapors are mildly narcotic and may result in a feeling of lethargy, drowsiness, and irritation of the eyes and mucous membrane. In one study, two males inhaled up to 16,680 mg butadiene/m³ for 8 hours without visible effects (Carpenter et al., 1944).

No reports of chronic effects arising from the industrial use of butadiene have been published in U.S. and Western Europe literature. Reports from Eastern Europe have suggested adverse effects from occupational exposure to butadiene, primarily in synthetic rubber manufacture. Poorly documented cases of gastrointestinal tract, and respiratory, circulatory and nervous system disorders have been reported.

Butadiene has a low toxicity in laboratory mammals. For mice and rats, the 2 hour LC₅₀ averages between 270,000 and 285,000 mg/m³ (Shugaev, 1969). Narcotic effects have been reported in mice exposed to 20% (200,000 mg/m³) butadiene in the air (Killian, 1930) and in rabbits exposed to 25% (250,000 mg/m³) (Carpenter et al., 1944). In a subacute study, rats

inhaling 0, 2200, 4400, 8800, or 18,000 mg/m³ for 6 hr/day, 5 days/week showed no signs of toxicity, except for a decrease in grooming behavior; however, some exposure groups showed a decrease in neuromuscular function, but not in a dose-dependent manner (Scala, 1977).

Chronic exposures of rats, rabbits, and guinea pigs to 1,326, 4,830, or 14,807 mg butadiene/m³ for 7.5 hr/day, 6 days/week for 8 months resulted in few changes (see Table 39). Although histological examination revealed no differences between treated and control animals, cloudy swelling of the liver was observed at the highest exposure level. Treated female rats had fewer litters compared to controls (Carpenter et al., 1944).

A series of Russian papers describes adverse effects in rats inhaling low levels of butadiene (0, 1, 3, or 30 mg/m³) continuously for 81 days (Ripp, 1967; Molodyuk, 1969; Nikiforova et al., 1969). Some of the reported effects at the highest level tested included: decreased weight gain after 50 days; leukocytosis; increased serum cholinesterase activity; decreased motor activity; and changes in the lung, spleen, kidney, and heart. In a long-term inhalation study, rats and rabbits exposed to 100 or 300 mg/m³ 4 hours/day for 4 months showed a lower leukocyte count and altered serum protein ratios (Batkina, 1966). A chronic gavage study in rabbits receiving 40 mg/kg for 7 months revealed lowered hemoglobin content (Shvartsapel, 1970).

One study in rats indicated that after inhalation, butadiene is found in the brain, liver, spleen, and particularly, the perinephric fat. Time sample measurements for the brain and liver indicated no traces of butadiene 90 minutes after exposure was terminated (Shugaev, 1969).

The mutagenic effect of butadiene was evaluated in 6 strains of Salmonella typhimurium by de Meester et al. (1978). Tests were performed both in the

absence and presence of a metabolic activation system. Two strains showed a direct (in absence of metabolic activation) and an indirect mutagenic response to butadiene.

Butadiene monoxide and diepoxybutane have been suggested as possible primary metabolites of butadiene (de Meester et al., 1978), but this has not been confirmed. Both butadiene monoxide and diepoxybutane have been shown to possess carcinogenic activity (Van Duuren et al., 1963; 1966), and diepoxybutane was mutagenic in several test systems (IARC, 1976b).

Little information is available on the toxicity of butadiene oligomers. Russian workers exposed to 4-vinylcyclohexene exhibited the following: keratitis, rhinitis, headache, hypotonia, leukopenia, neutrophilia lymphocytosis and impaired metabolism (Bykov, 1968 in IARC, 1976a). The oral LD₅₀ of vinylcyclohexene in rats is 3.08 ml/kg (2,556 mg/kg). It caused irritation when applied to rabbit skin (Smyth et al., 1969), and also produced skin tumors when similarly applied but this latter effect may have been due to contamination of the sample with the hydroperoxide of vinylcyclohexene (Van Durren, 1963; 1965). Cyclooctadiene and cyclododecatriene caused sensitization and severe contact dermatitis when applied to the skin of laboratory mammals (Brown and Hunter, 1968).

In plants, fumigation with butadiene resulted in no injury at 10 ppm (22.1 mg/m³) and <5% injury at 100 or 1,000 ppm (2210 mg/m³) (Heck and Pires, 1962). Exposure to plants to mixtures of butadiene and ozone and the irradiation products of butadiene and nitrogen oxides usually resulted in typical smog damage (Haagen-Smit, et al., 1952).

Occupational exposure to butadiene is limited by the Occupational Safety and Health Administration to an 8-hour time-weighted average of 1,000 ppm (2,200 mg/m³). The Department of Transportation regulates the transport of

butadiene. The Environmental Protection Agency has set effluent limitation guidelines for discharges associated with butadiene manufactured by oxidative dehydrogenation. Butadiene is regulated as an indirect food additive by the Food and Drug Administration.

BIBLIOGRAPHY

- Abdullaeva, R. G., (1973) ("Differentiated Study of the Disease Rate of Workers at a Synthetic Rubber Plant (According to Clinical Data)") Tr. Azerb. Nauchnoissled. Inst., Gig, Tr. Prof. Zabol., 8:145-8 (Russian); Chem. Abstr. 82:47351y.
- Abeles, F. B., and Gahagan, H. E., (1968) "Abscission: The Role of Ethylene, Ethylene Analogs, Carbon Dioxide, and Oxygen," Plant Physiol., 43:1255-1258.
- ACGIH, (1971) Documentation of the Threshold Limit Values for Substances in Workroom Air, 3rd. Edit., Cincinnati, Ohio, p. 28.
- ACGIH, (1977) Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH for 1977, Cincinnati, Ohio.
- Adams, S. I., (1977) "Analysis of Combustion Gases During Testing with the NBS Smoke Chamber," J. Combust. Toxicol., 4:360-366.
- Alekperov, I. I., Knabengof, V. G. and Vinokorova, M. I., (1968) ("Capillaro-scopic Studies and Determination of the Stability of Capillaries in Persons Working with 1,3-Butadiene, Styrene, and Ethylbenzene,") Azerb. Med. Zh., 45:58-61 (Russian); Chem. Abstr. 80:80662a.
- Alekeperov, I. I., Knabengof, V. G., Vinokurova, M. I., (1971) ("Oscillo-graphic Study of Vessel Tone and Hemodynamics of Persons Working with Petroleum Hydrocarbons") Tr. Azerb. Nauch. - Issled. Inst. Gig., Tr. Prof. Zabol., 5:22-30 (Russian); Chem. Abstr. 81:67971h.
- Alekperov, I. I., Vinokurova, M. I., Knabengof, V. G., (1970) ("Combined Ef-fect of Styrene, Butadiene and Ethylbenzene on the Contractile Function of the Myocardium") Tr. Azerb. Nauch. - Issled. Inst. Gig. Tr. Prof. Zabol., 5:46-55 (Russian); Chem. Abstr. 81:67973k.
- Allen, P. W., (1972) Natural Rubber and the Synthetics, John Wiley & Sons, N.Y.
- Almemmingen, A., Bastiansen, O., and Traetteberg, M., (1958) "An Electron Dif-fraction Reinvestigation of the Molecular Structure of 1,3-Butadiene," Acta. Chem. Scand., 12:1221-1225.
- Altschuller, A. P., Klosterman, D. L., Leach, P. W., Hindawi, I. J., and Sigsby, J. E., (1966) "Products and Biological Effects from Irradiation of Nitrogen Oxides with Hydrocarbons or Aldehydes Under Dynamic Conditions," Int. J. Air & Water Pollut. 10:81-98.
- Altschuller, A. P., Lonneman, W. A., Sutterfield, F. D. and Kopczynski, S. L., (1971) "Hydrocarbon Composition of the Atmosphere of the Los Angeles Basin-1967," Environ. Sci. & Tech., 5(10):1009-1016.
- AMOCO Chemicals Corp., (1978) personal communication with H. G. Twaddle, Toxicity Regulations coordinator.
- Anon., (1971) "Butadiene," Hydroc. Proc., Nov. 1971:137.
- Anon., (1972) "Perspective," Chem. Age, Aug. 4, 1972:13-14.

- Anon., (1976a) "Butadiene Production US," Chem. Eng., August 2, 1976:46.
- Anon., (1976b) "Butadiene," Chem. Eng. News, Nov. 15, 1976:16.
- Anon., (1976c) "Chemical Profile: Polybutadiene," Chem. Mark. Rep., 210(21):9.
- Anon., (1976d) "Chemical Profile: Neoprene," Chem. Mark. Rep., 210(7):9.
- Anon., (1976e) "Chemical Profile: Nitrile Rubber," Chem. Mark. Rep., 210(7):9.
- Anon., (1976f) "Petro-Tex Will Shutter Houdry Butadiene Units," Chem. Mark. Rep., Dec. 20, 1976:5.
- Anon., (1977a) "Chemical Profile: Butadiene," Chem. Mark. Rep., 211(23):9.
- Anon., (1977b) "Gulf Coast Draws Flurry of Processing Projects," Oil Gas J., June 27, 1977:68.
- Anon., (1977c) "Checkoff-Butadiene," Chem. Eng. News, Oct 21, 1977:9
- Anon., (1977d) "Ethylene," Hydrocarbon Process, Nov. 1977:154.
- Anon., (1977e) "Key Chemicals: Butadiene," Chem. Eng. News, Nov. 7, 1977:14.
- Anon., (1977f) "Slower Demand Growth Seen for Olefins," Oil Gas J., May 16, 1977:50-51.
- Anon., (1977g) "Butadiene Supply Lags World Demand," Rubber World, 176(5):23.
- Anon., (1977i) "Chemical Profile: SBR," Chem., Mark. Rep., 211(11):9.
- Anon., (1977j) "Chemical Profile: ABS Resins," Chem. Mark. Rep., 211(13):9.
- Anon., (1977k) "Cis-Polybutadiene," Hydrocarbon Process, Nov., 1977:199.
- Anon., (1977l) "Plastics Corner," J. Commer., March 3, 1977:5.
- Anon., (1977m) "ABS '77: New Supplier, New Supplier, New Grade, 100,000-Plus Tons of New Capacity," Mod. Plast., 54(2):16.
- Anon., (1977n) "ABS Project Scheduled," Chem. Mark. Rep. 211(22):2.
- Anon., (1978a) "World Butadiene Growth Holds at 2.5% Annually," Chem. Eng. News, May 29, 1978:5.
- Anon., (1978b) "Capacity Use Still Slips in Basic Chemicals," Chem. Eng. News, Mar. 6, 1978:9-10.
- Anon., (1978c) "World Wide HPI Construction Boxscore," Hydroc. Proc. February 1978:35.

Anon., (1978d) "51. Canada," International Environment Reporter, Bureau of National Affairs, Inc., Washington, D.C.

ASTM (1975) Annual Book of ASTM Standards, Phila., Pa.

Babanov, G. P., (1960) ("Problems of Industrial Hygiene in the Production of Synthetic Butadiene-Acrylonitrile Rubbers,") Gig. Tr. Prof. Lab., 4(12):7-12 (Russian).

Bailey, W. J., (1971) "Butadiene," in Leonard, E. C. Vinyl and Diene Monomers, part 2, Wiley-Interscience, N.Y., pp. 757-995.

Bashirov, A. A., (1968) ("Functional State of the Liver in Chronic Gastric Diseases in Workers of the Divinyl and Styrol Industry,") Vrach. Delo., 12:92-94 (Russian).

Bashirov, A. A., (1969) ("Functional Changes in Endocrine Glands Due to Butadiene and Styrene,") Gig. Tr. Prof. Zabol., 13(7):40-41 (Russian).

Bashirov, A. A., (1970) ("Effect of Histamine on the Stomach in Antacid Gastritis in Subjects Occupationally Exposed to Aromatic Hydrocarbons") Ter. Arkh., 42:41-42 (Russian); Chem. Abstr., 74:138804z.

Bashirov, A. A., (1971) ("Blood Serum Protein Composition and Diseases of the Digestive Organs in Persons Exposed to Divinyl and Styrene,") Gig. Tr. Prof. Zabol., 15(5):57-59 (Russian).

Bashirov, A. A., (1973) ("Relation Between Excretory Function of the Liver and Secretory Function of the Stomach in People Working with Petroleum Hydrocarbons,") Azerb. Med. Zh., 50(12):62-66 (Russian).

Batkina, I. B., (1966) ("On the Maximum Permissible Concentration of Divinyl Vapor in the Air in Work Areas,") Gig. Sanit., 31(12):18-22 (Russian).

Bauchwitz, P. S., Finlay, J. B. and Stewart, C. A., (1971) "Chloroprene" in Leonard, E. C. Vinyl and Diene Monomers, part 2, Wiley Interscience, N.Y., pp. 1149-1183.

Bellringer, F. J. and Hollis, C. E., (1968) "Make Chloroprene from Butadiene," Hydroc. Proc., 47(11):127-130.

Bengelsdorf, I. S., Nudenberg, W. and Li, H. J., (1960) "The Diels-Alder Dimer of Butadiene: 4-Vinyl-1-Cyclohexene," Texas-U.S. Chemical Co., Port Neches, Texas, 32 pp.

Bock, K. J. and Elm, H., (1974) ("Technology and Environmental Protection: Butadiene Recovery from Rubber as a Good Example,") Lichtbogen, 23(175):6-9 (German).

Bordo, J. A., (1951) ("Sewage Purification in a Chemical Operation,") Wasserwirtschaft, 41:239-246 (German).

Brown, V. K. H. and Hunter, C. G., (1968) "Experimental Studies on Skin Hazard with Cycloocta-1,5-Diene and Cyclododeca-1,5,9-Triene," Br. J. Ind. Med., 25:75-76.

Brownstein, A. M., (1976) "Butadiene: A Viable Raw Material," Hydrocarbon Process, Feb. 1976:95-98.

Bruzzone, M., (1974) "Make this New EDM Copolymer," Hydrocarbon Process, May, 1973:153-154.

Buchoff, L. S., (1975) "Liquid and Low-Pressure Resin Systems," in Harper, C.A. (ed.) Handbook of Plastics and Elastomers, McGraw-Hill Book Co., N.Y., pp. 8-51.

Bul'bakov, K. S., (1969) ("Pathomorphology of the Heart During the Chronic Action of α -Methylstyrene and 1,3-Butadiene Mixtures on Animals") Nauch. Tr. Omsk. Med. Inst., 88:269-73 (Russian); Chem. Abstr. 75:96881k.

Burg, S. P. and Burg, E. A., (1966) "Molecular Requirements for the Biological Activity of Ethylene," Plant Physiol., 42:144-152.

Candlin, J. P. and Janes, W. H., (1968) "The Catalytic Dimerisation of Dienes by Nitrosylcarbonyl Transition-Metal Compounds," J. Chem. Soc. (C):1856-1860.

Carpenter, C. P., Shaffer, C. B., Weil, C. S. and Smyth, H. F., Jr., (1944) "Studies on the Inhalation of 1:3-Butadiene; with a Comparison of Its Narcotic Effect with Benzol, Tolnol and Styrene, and a Note on the Elimination of Styrene by the Human," J. Indus. Hyg. and Toxicol., 26(3):69-78.

Carson, J. W. and Lege, G. J., (1974) "Butadiene Dimer Formation in Chromatograph Vaporizers," J. Chromatogr. Sci., 12:49-50.

Carson, J. W., Young, J. D., and Lege, G., (1972) "An Improved Column by Butadiene Analysis," J. Chromatogr. Sci., 10:737-740.

Case, R. A. M. and Hosker, M. E., (1954) "Tumor of the Urinary Bladder as an Occupational Disease in the Rubber Industry in England and Wales," Br. J. Prev. Soc. Med 8:39-50.

Chase, J. W., (1978) Technical Information Specialist, National Cancer Institute, Bethesda, Md., written communication.

CHRIS (1974) Hazardous Chemical Data, Department of Transportation, Coast Guard, CG-446-2.

Chukreev, E. F., (1969a) ("Effect of the Long-Term of Small Concentrations of α -Methylstyrene Alone and Mixed With 1,3-Butadiene on the Cholesterol Level in the Serum of Animals") Nauch. Tr., Omsk. Med. Inst., 88:261-4 (Russian); Chem. Abstr., 75:96903u

Chukreev, E. F., (1969b) ("Effect of the Long-Term Action of Small Concentrations of α -Methylstyrene Alone and Mixed With 1,3-Butadiene on the Cholesterol Level in the Liver of Animals") Nauch. Tr., Omsk. Med. Inst., 88:265-8 (Russian); Chem. Abstr., 75:107720k.

Citco, (1969) New Products Bulletins: 4-Vinylcyclohexene-1; 1,5,9-Cyclododecatriene; 1,5-Cyclooctadiene, Cities Service Co., Houston, Texas.

Citco, (1978) Specialty Products Availability and Price Schedule, Cities Service Co., written communication.

Coffey, S., (1968), Roods Chemistry of Carbon Compounds, 2nd Ed., Elsevier Pub. Co., N.Y., pp. 383-387

Coker, D. T., (1977) "Heat Desorption of Vapour-Trapping Tubes," Proc. Analyt. Div. Chem. Soc., 14:108-109.

Cunningham, S. A., (1971) "Oxidative Dehydrogenation By-Product Elimination," U.S. Patent 3,557,238.

Day, D. C., (1975) "Liquid Effluents-Emission Points from Rubber Manufacturing Process," in Environmental Aspects of Chemical Use in Rubber Processing Operations, Research Triangle Institute Contract No. 68-01-2928.

Debreczeni, E. J., (1977) "Future Supply and Demand for Basic Petrochemicals," Chem. Eng., June 6, 1977:135-141.

De Meester, C., Poncelat, F., Roberfroid, M. and Mercier, M., (1978) "Mutagenicity of Butadiene and Butadiene Monoxide," Biochem. Biophys. Res. Comm., 80(2):298-305.

Dept. of Commerce, (1977)" Rubber: Supply and Distribution for the United States," MA-30A(76)-1.

DiCorcia, A. and Samperi, R., (1975) "Evaluation of Modified Graphitized Carbon Black for the Analysis of Light Hydrocarbons," J. Chromatogr., 107:99-105.

DiCorcia, A., Samperi, R. and Capponi, G., (1977) "Impurity Analysis in Pure-Grade 1,3-Butadiene," Chromatographia, 10(9):554-555.

Donetskaya, E. I. and Shvartsapel, F. S., (1970) ("Morphological Studies of the Organs of White Rats Under the Action of 1,3-Butadiene in Subacute Experiments,") Tr. Permsk. Med. Inst., 82:223-225 (Russian).

Drinkard, W. C., (1970) "Addition of Hydrogen Cyanide to Butadiene," U.S. Pat. 3,547,972.

Driver, Y., (1976) "What Price Butadiene?" Hydrocarbon Process, May 1976:143-145.

EPA, (1974a) Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Tire and Synthetic Segment of the Rubber Processing Point Source Category, EPA-440/1-74-013-9.

EPA, (1974b) Major Organic Products Segment of the Organic Chemicals Manufacturing, Point Source Category, EPA-440/1-74-009-a.

Ericsson, R. L., (1976) "Butadiene-Coproduct Versus Dehydro," Meeting Paper 37c, AIChE, Atlantic City, N.J., 9/1/76, 15 pp.

- Ericksson, R. L. (1977) "Butadiene," manuscript submitted for publication, personal communication, 33 pp.
- Exxon (1973) "Specifications: Butadiene," Exxon Chemical Co., Houston, Tx.
- Exxon, (1974) "Storing and Handling Liquified Olefins and Diolefins," CRM-74-1685, Exxon Chem Co., Houston, Tx. 18 pp.
- Exxon, (1977) "Material Safety Data Sheet: Butadiene," Exxon Chemical Co., Houston, Tx.
- Fadeeva, Z. M. and Eikhler, Y. N., (1977) ("Experimental Data on the Combined Effect of Divinyl and Alpha-methylstyrene on the Animal Organism") Nauk. Tr. Omsk. Med. Inst., 107:166-174 (Russian).
- Faustov, A. S., (1972) ("Toxic Conditions in the Production of Synthetic Rubbers") Tr. Voronezh. Med. Inst., 87:10-16 (Russian); Chem. Abstr. 80:63410d.
- Faustov, A. S. and Lobeeva, N., (1970) ("Action of Some Chemical Substances on the Protein Content of Serum and Bone Marrow,") Gig. Sanit., 35(8):112-113 (Russian).
- Fine, L. J. and Peters, J. M., (1976a) "Respiratory Morbidity in Rubber Workers," Arch. Env. Health., Jan/Feb:5-9.
- Fine, L. J. and Peters, J. M., (1976b) "Studies of Respiratory Morbidity in Rubber Towkers," Arch. Env. Health, May/June:136-140.
- Firestone (1977). Annual Report: Firestone Tire and Rubber Co., Akron, Ohio.
- Firestone (1978) Personal communication with Joe Laman.
- Fox, A. J., Lindars, D. C., and Owen, R., (1974) "A Survey of Occupational Cancer in the Rubber and Cablemaking Industries: Results of Five-Year Analysis, 1967-71," Br. J. Ind. Med. 31:140-151.
- Fuller, B., Hushon, J., Kornreich, M., Quellette, R., Thomas, L. and Walker, P. (1976) "Preliminary Scoring of Selected Organic Air Pollutants," EPA-450/3-77-008a.
- Garrett, J. T., (1957) "Toxicity Considerations in Pollution Control," Ind. Wastes. Jan-Feb., 1957:17-19.
- Glasson, W. A., and Tuesday, C. S., (1970a) "Hydrocarbon Reactivities in the Atmospheric Photooxidation of Nitric Oxide," Env. Sci. Technol., 4(11):916-924.
- Glasson, W. A. and Tuesday, C. S., (1970b) "The Atmospheric Thermal Oxidation of Nitric Oxide in the Presence of Dienes," Environ. Sci. Tech., 4(9):752- 757.
- Gloyna, E. F., and Ford, D. L., (1970) The Characteristics and Pollutational Problems Associated with Petrochemical Wastes, NTIS Report PB-192310.

Greene, K. and Pennington, R. E., (1977) "Butadiene," Meeting Paper 8e, AIChE, Houston, Texas., 3/21/77, 11 pp.

Gunther, B. J. and Lucas, J. B., (1973) Health Hazard Evaluation/Toxicity Determination, NTIS PB-229508.

Gus'kova, K. P., (1971) ("Effect of Occupational Factors in the Production of Synthetic Rubber on the Nervous System of Workers in Some Shops") Nauch. Tr., Omsk. Med. Inst., 107:88-94 (Russian); Chem. Abstr. 78:8831d.

Haagen-Smit, A. J., Darley, E. F., Zaitlin, M., Hull, H., and Noble, W., (1952) "Investigation on Injury to Plants from Air-Pollution in the Los Angeles Area," Plant. Physiol., 27:18-34.

Hammond, G. S., Turro, N. J. and Fischer, A., (1961) "Photosensitized Cyclo-Addition Reactions," J. Am. Chem. Soc., 83:4674-4675.

Hammond, G. S., Turro, N. J. and Liu, R. S. H., (1963) "Mechanisms of Photochemical Reactions in Solution. XVI. Photosensitized Dimerization of Conjugated Dienes," J. Org. Chem., 28:3297-3303.

Hanst, P. L., Stephens, E. R., Scott, W. E. and Doerr, R. C. (1959) "Atmospheric Ozone-Olefin Reactions," Am. Chem. Soc. Div. Petrol. Chem. Preprints, 4(4):7-16.

Hazardous Materials Transportation Act, P.L. 93-633, Approved January 3, 1975.

Hargreaves, C. A., (1968) "Elastomers by Radical and Redox Mechanisms: C. Neoprene," in Kennedy, J. P. and Torquist, E. Polymer Chemistry of Synthetic Elastomers, Part 1, Interscience Pub., N.Y., pp. 227-252.

Heck, W. W. and Pires, G., (1962) "Growth of Plants Fumigated with Saturated and Unsaturated Gases and Their Derivatives," Texas Agr. Expt. Sta. Misc. Publ. MP-603, 12 p.

Henderson, R. M., (1978) Manager, Retrochemical Sales, Cities Service Co., written communication.

Heuss, J. M. and Glasson, W. A., (1968) "Hydrocarbon Reactivity and Eye Irritation," Environ. Sci. Tech., 2(12):1109-1116.

Hillyer, J. C. and Stallings, P. S., (1956) "Growing Fast-Butadiene Material of the Future," Pet. Refiner, 35(12):157-163.

Hinton, R. A., and Cottle, J. E., (1972) "Purification of Oxidative Dehydrogenation Process Effluents," U.S. Patent 3,679,764.

Hutson, T. and Riter, R. E., (1972) "Enzymatic Treatment of Hydrocarbon Dehydrogenation Effluent," U.S. Patent 3,646,239.

Hutson, T., Skinner, R. D. and Logan, R. S., (1974) "Phillips' New Butadiene Process," Hydrocarbon Process, June, 1974:133-135.

Huybrechts, G., Luyckx, L., Vandenboom, T. H. and VanMele, B., (1977) "Thermal Dimerization of 1,3-Butadiene: Kinetics of the Formation of Cis, Cis-Cycloocta-1,5-Diene," *Int. J. Chem. Kinet.*, 9:283-293.

IARC, (1976a) "4-Vinylcyclohexene," IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man, Vol 11, pp. 277-281.

IARC, (1976b) "Diepoxybutane," IARC Monograph on the Evaluation of Carcinogenic Risk of Chemicals to Man, Vol 11, pp 115-123.

ITII, (1975) Toxic and Hazardous Industrial Chemicals Safety Manual, International Technical Information Institute, Tokyo, p. 82-83.

Johnson, H. L., (1949) "Dimerization of Butadiene," U.S. Patent 2,468,432.

Kennedy, D., (1977) "Indirect Additives: Polymers. Acrylonitrile Copolymers Used to Fabricate Beverage Containers," Final Decision," *Fed. Regist.*, 42(185):48528-48544.

Khusainova, F. A., (1971) ("Peripheral Blood Indexes in Workers Employed in the Production of Butadiene- α -Methylstyrene Rubber") *Tr. Azerb. Nauch.-Issled. Inst. Gig. Tr. Prof. Zabol.*, 7:172-5 (Russian); *Chem. Abstr.* 78:88310v.

Killian, H., (1930) ("Studies on the Higher Gas Narcotics of the Hydrocarbon Series,") *Schmerz Nark.-Anaest.*, 3:121-159 (German).

Kirshenbaum, I. and Cahn, R. P., (1964) "Butadiene," *Kirk-Othmer Encycl. Chem. Technol.*, 3:784-815.

Kiltleson, A. R., (1951) "Parasitical Compounds Containing the NSCCl₃ Group," U.S. Patent 2,553,770.

Klaus, M., (1977) "Prospects of the Petrochemical Industry in the World-Its Feedstocks, Problems and Projects," *Chem. Econ. Eng. Rev.* 9(4):7-16.

Klein, O., et al., (1967) ("Investigation of State of Health and Evaluation of Growth of Juveniles in a Styrene-Butadiene-Rubber Plant,") *Cekskosl. Hyg.*, 12(9):514-520 (Czech).

Konstantinovskaya, A. S., (1970) ("The Renal Function in Workers Employed in the Production of Divinyl-Alpha-Methylstyrene Rubber,") *Gig. Truda I Prof. Zabol.*, 14:10-12 (Russian).

Konstantinovskaya, A. S., (1971) ("State of the Coronary Vessel System of Workers in Butadiene-Methylstyrene Rubber Production") *Vop. Gig. Tr. Prof. Zabol., Mater. Nauch, Konf.* 1971:194-6 (Russian); *Chem. Abstr.* 81:140388e.

Kreuzer, L. B., Kenyon, N. D. and Patel, C. K. N., (1972) "Air Pollution" Sensitive Detection of Ten Pollutant Gases by Carbon Monoxide and Carbon Dioxide Lasers," *Science*, 177:347-349.

Kuz'min, V. I., (1969) ("Pathomorphological Changes in the Lungs of White Rats Under the Action of 1,3-Butadiene and α -Methylstyrene Vapors,") Nauch. Tr., Omsk. Med. Inst. 88:215-19 (Russian); Chem. Abstr. 75:107749b.

Lambina, S. A., (1969a) ("Changes in the Level of Ribonucleoproteins and Total Protein in the Liver of Rats Under the Effect of Chronic Inhalation Priming with a Mixture of 1,3-Butadiene and α -Methylstyrene,") Nauch. Tr., Omsk. Med. Inst., 88:179-84 (Russian); Chem Abstr 75:107780e.

Lambina, S. A., (1969b) ("Dynamics of the Level and Distribution of Glycogen and Lipids in the Liver of Rats Under the Effect of Chronic Inhalation Priming with a Mixture of 1,3-Butadiene and α -Methylstyrene") Nauch. Tr., Omsk. Med. Inst. 88:174-8 (Russian); Chem. Abstr. 75:107779m.

Lefaux, R., (1968) Practical Toxicology of Plastics, CRC Press, Cleveland, Ohio, 580 pp.

LiGotti, I., Franzosi, M. and Bonomi, G., (1972) ("Determination of Free Butadiene Rubbers," Mater. Plast. Elastomeri, 38(2):142-143 (Italian).

Liu, D., (1978) CTC Organics, Atlanta, Ga., personal communication.

Liu, R. S. H., Turro, N. J., Jr., and Hammond, G. S., (1965) "Mechanisms of Photochemical Reactions in Solution. XXXI. Activation and Deactivation of Conjugated Dienes by Energy Transfer," J. Am. Chem. Soc. 87(15):3406-3412.

Lowenheim, F. A. and Moran, M. K., (1975) Faith, Keyes, and Clark's Industrial Chemicals, 4th edition, Wiley-Interscience, N.Y., pp. 164-172.

Lukoshina, L. P. et al., (1973) ("The Status of Lipid-Protein Metabolism in Workers with Divinyl and Styrene,") Gig. Sanit., 17(8):42-44 (Russian).

Lyashenko, K. S. and Sidenko, A. T., (1974) ("Improvement of Working Conditions in the Manufacture of Dimethyl Terephthalate,") Gig. Tr. Prof. Zabol. 1974(9):42-43 (Russian).

Madorsky, S. L., (1964) "IX. Polybutadiene and Copolymers of Butadiene with Styrene and Acrylonitrile," Thermal Degradation of Organic Polymers, Interscience Publ., N.Y., 203-212.

Mancuso, T. F., Giocco, A., and El-Attar, A. A., (1968) "An Epidemiological Approach to the Rubber Industry," J. Occup. Med., 10(5):213-232.

Manita, M. D. and Ripp, G. K., (1965) "Spectrophotometric Determination of Low Atmospheric Concentrations in the Presence of Other Products Liberated During the Manufacture of Synthetic Rubber," Hyg. Sanit., EPA & NSF, (Gig. Sanit.) 30:231-234.

MCA, (1966) Case Histories of Accidents in the Chemical Industry, Volume 2, Washington, D. C., p 79.

MCA, (1974) "Chemical Safety Data Sheet SD-55. Properties and Essential Information for Safe Handling and Use of Butadiene," Manufacturing Chemists Association, Wash., D.C.

McAuliffe, C., (1966) "Solubility in Water of Paraffin, Cycloparaffin, Olefin, Acetylene, Cycloolefin & Aromatic Hydrocarbons," J. Phys. Chem., 70:1267-1275.

McCormick, W. E., (1971) "Environmental Health Control for the Rubber Industry," Rubber Chem. & Tech., 44:512-532.

McMichael, A. J., Spiritas, R., Gamble, J. F., and Tousey, P. M., (1976) "Mortality Among Rubber Workers: Relationship to Specific Jobs," J. Occup. Med., 18(3):178-185.

Mirzoyan, I. M., and Tsai, L. M., (1971) ("Working Conditions and Hygienic Study of the Polymerization Works of the Karaganda Synthetic Rubber Plant" Vop. Gig. Tr. Prof. Zabol., Mater. Nauch. Knof., 1971:25-2 (Russian); Chem. Abstr. 81:110878x.

Molodyuk, A. V., (1969) ("Histological and Histochemical Changes in Tissue Components of Hematogenic Organs of Experimental Animals During the Action of α -Methylstyrene and 1,3-Butadiene Vapors,") Nauch. Tr., Omsk. Med. Inst., 88:231-9 (Russian); Chem. Abs. 75:116947s.

Morikawa, H., Sagara, M. and Kakemoto, G., (1972) "CDT/CD from C4 Fractions," Hydrocarbon Process, August, 1972:102-104.

Morozov, G. I., (1969a) ("Morphological Changes in the Internal Sex Organs of Female White Rats During the Action of Vapors of α -Methylstyrene Alone and Mixed With 1,3-Butadiene on the Animals") Nauch. Tr., Omsk. Med. Inst., 88:254-60 (Russian); Chem. Abstr. 75:96902t.

Morozov, G. I., (1969b) ("Morphological Changes in White Rat Testicles During the Action of α -Methylstyrene and 1,3-Butadiene Vapors on the Animals") Nauch. Tr., Omsk. Med. Inst., 88:249-53 (Russian); Chem. Abstr., 75:96900r.

Neligan, R. E., (1962) "Hydrocarbons in the Los Angeles Atmosphere," Arch. Environ. Health, 5:67-77.

Nemphos, S. P., Salame, M. and Steingiser, S., (1976) "Barrier Polymers," in Encycl. Polymer Sci. Technol., 1(Suppl.):65-95.

Nikiforova, A. A., Ripp, G. K., and Taskev, I. I., (1969) ("Action of 1,3-Butadiene on the Structural Elements of the Kidneys and Heart,") Nauch. Tr. Omsk. Med. Inst., 88:166-169 (Russian).

NIOSH (1975) "NIOSH Analytical Methods for Set G," NTIS Rep. PB-246-150/AS.

NIOSH, (1976) "Proceedings of NIOSH Styrene-Butadiene Briefing," U.S. Dept. H.E.W., Cincinnati, Ohio.

Occupational Safety and Health Administration Act of 1970, P. L. 91-596, Approved December 29, 1970.

Ono, I. and Kihara, K., (1967) "New Process Makes COD and CDT," Hydroc. Proc., 46(8):147-150.

Orlova, A. A. and Solov'eva, E. A., (1962) ("Clinical Picture of Chronic Exposure to Various Chemicals Used in Synthetic Rubber") Tr. Voronezhsk, Med. Inst., 47:86-7 (Russian); Chem. Abstr. 61:1169h.

Osborne, J. S., Adamek, S. and Hobbs, M. E., (1956) "Some Components of the Gas Phase of Cigarette Smoke," Anal. Chem., 28(2):211-215.

Oura, E., Raima, N. C. R. and Suomalaine, H., (1966) "Influence of Some Alcohols and Narcotics on the Adenosine Phosphates in the Liver of the Mouse," Ann. Med. Exp. Fenn., 45:57-62.

Parsons, T. B., Thompson, C. M., and Williams, G. E., (1977) "Industrial Process Profiles for Environmental Use: Chapter 5. Basic Petrochemicals Industry," EPA-600/2-77-023e.

Parsons, T. B. and Wilkins, G. E., (1976) "Biological Effects and Environmental Aspects of 1,3-Butadiene," EPA-560/2-76-004 52 pp.

Pervier, J. W., Barley, R. C., Field, D. E., Friedman, B. M., Morris, R. B. and Schwartz, W. A., (1974a) "Styrene-Butadiene Rubber" in Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume IV, NTIS Rep. PB-244-957.

Pervier, J. W., Barley, R. C., Field, D. E., Friedman, B. M., Morris, R. B., and Schwartz, W. A., (1974b) "Adyponitrile via Butadiene" in Survey Reports on Atmospheric Emissions from the Petrochemical Industry, Volume I, NTIS Rep. PB-244-957.

Peters, W. D. and Rogers, R. S., (1968) "Improved Furfural Extraction Process," Hydrocarbon Process, 47(11):131-134.

Petro-Tex (n.d.) "Material Safety Data Sheet: Butadiene" Houston, Texas.

Petro Tex (1978) William Taylor, Manager, Marketing & Hydrocarbon Supply, Petro-Tex Chemical Corp., Houston, Tx., written communication.

Prescott, J. H., (1976) "Butadiene's Question Mark," Chem. Eng., Aug. 2, 1976:46-50.

Pruessner, R. D. and Mancini, J., (1966) "Extended Aeration Activated Sludge Treatment of Petrochemical Waste at the Houston Plant of Petro-Tex Chemical Corporation," Proc. 21st Ind. Waste Conf. Part 1. pp 591-599.

Purcell, T. O. (1976) "Methyl Methacrylate-Butadiene-Styrene Terpolymers," in Encycl. Polymer Sci. Technol., 1(Suppl.):319-325.

Rappaport, S. M. and Fraser, D. A., (1977) "Air Sampling and Analysis in a Rubber Vulcanization Area," Am. Ind. Hyg. Assoc. J., 38:205-210.

Reed, H. W. B., (1954) "The Catalytic Cycle Polymerization of Butadiene," J. Chem. Soc., 1954:1931-1941.

Ripp, G. K., (1967) ("Hygienic Basis for the Permissible Concentration of Butadiene in the Atmosphere,") Biol. Deislvie Gig. Znachenie Atmos. Zagryaznenii, 1967(10):33-54 (Russian).

Ripp, G. Kh., (1969) ("Toxicohygienic Characteristics of 1,3-Butadiene,") Nauch. Tr. Omsk. Med. Inst., 88:10-18 (Russian).

Rodde, A. L. (1978) Manager New Product Sales Development, Texas U.S. Chemical Co., written communication.

Saltman, W. M., (1965) "Butadiene Polymers," Kirk-Othmer Encycl. Chem. Technol., 2:678-754.

Scala, R. A., (1977) "Toxicology of Butadiene," Meeting Paper, A.C.S. Rubber Division Symposium—Occupational Health in the Rubber Industry, 10/6/77, 10 pp.

Seinfeld, J. H. (1975) Air Pollution: Physical and Chemical Fundamentals, McGraw-Hill, Inc., 159-217.

Serebrennikov, O. A., (1969) ("Renin Level in Kidneys of Experimental Animals During Chronic Poisoning with a Mixture of α -Methylstyrene and 1,3-Butadiene,") Nauch. Tr., Omsk. Med. Inst., 88:244-8 (Russian); Chem. Abstr. 75:107797r.

Shapras, P. and Claver, G. C., (1964) "Determination of Residual Monomers and Other Volatile Components in Styrene Based Polymers by Gas Chromatography," Anal. Chem., 36(12):2282-2283.

Shuartsapel, F. S., (1970) ("A Study of the Toxic Properties 1,3-Butadiene in Chronic Experiments,") Tr. Perm. Med., Inst., 82:174-179 (Russian).

Shugaev, B. B., (1969) "Concentrations of Hydrocarbons in Tissues as a Measure of Toxicity," Arch. Environ. Health, 18:878-882.

Siddiqi, A. A. and Worley, F. L., Jr., (1977) "Urban and Industrial Air Pollution in Houston, Texas—I. Hydrocarbons," Atmos. Environ., 11:131-143.

Simpson, C., (1978) Products Development, DuPont, Wilmington, Del., personal communication.

Singer, S. A., (1976) "Economic Analysis of Effluent Guidelines: The Primary 1,3-Butadiene Subcategory of the Organic Chemical Industry," EPA-230/2-74-042a. 91 pp.

Skuja, K., (1969) ("Combined Effect of Butadiene and Toluene on the Rat Estrous Cycle,") Akush. Ginekolog., 45:67-68 (Russian).

Slater, D. H., (1978) "Vapor Clouds," Chem. Ind., May 6, 1978:295-302.

Smith, A. H. and Ellis, L., (1977) "Styrene Butadiene Rubber Synthetic Plants and Leukemia," J. Occup. Med., 19(7):441.

Smyth, H. F., Jr., Carpenter, C. P., Weil, C. S., Pozzani, U. C., Striegel, J. A. and Nycum, J. S., (1969) "Range-Finding Toxicity Data: List VII," *Am. Ind. Hyg. J.*, Sept.-Oct., 1969:470-476.

Sopach, E. D. and Krotova, Z. A., (1973) ("Study of the Behavior of Divinyl Rubbers and their Destruction Products in Aqueous Solutions,") *Gig. Sanit.*, 38(8):94-95 (Russian).

SRI, (1975 and 1977) *Directory of Chemical Products-U.S.A.* Stanford Research Institute, Menlo Park, Calif.

Srinivasan, R., (1966) "Photochemistry of Conjugated Dienes and Trienes," in Noyes, W. A., Jr., Hammond, G. S. and Pitts, J. N., Jr. (eds.) Advances in Photochemistry Volume 4. John Wiley & Sons, New York, pp. 113-142.

Srinivasan, R. and Sonntag, F. I., (1965) "Energy Level of the First Excited Singlet State of 1,3-Butadiene," *J. Am. Chem. Soc.*, 87(16):3778-3779.

Stahley, E. F., (1951) "Dimerization of Butadiene," U.S. Patent 2,544,808.

Steere, N. V., (ed.), (1968) "Safety in the Chemical Laboratory. XLVI. Hazardous Chemicals Data," *J. Chem. Educ.*, 45(3):4199-4205.

Steichen, R. J., (1976) "Modified Solution Approach for the Gas Chromatographic Determination of Residual Monomers by Head-Space Analysis," *Anal. Chem.*, 48(9):1398-1402.

Stephens, E. R. and Burleson, F. R., (1967) "Analysis of the Atmosphere for Light Hydrocarbons," *J. Air Pollut. Control Assoc.*, 17(3):147-153.

Takeuchi, Y., Sekimoto, A. and Abe, M., (1974a) "A New Thermoplastic Syndiotactic 1,2-Polybutadiene. I Production, Fundamental Properties, and Processing" in Denin, R. D. (ed.) New Industrial Polymers, ACS Symposium Series 4, Washington, D.C., pp. 15-25.

Takeuchi, Y., Sekimoto, A. and Abe M., (1974b) "A New Thermoplastic Syndiotactic 1,2-Polybutadiene. II. Applications, in Deanin, R. D. (ed.) New Industrial Polymers, ACS Symposium Series 4, Washington, D.C. pp 26-36.

Texas U.S. Chemical Co. (1978) Personal communication with D. J. Rivette, Environmental Engineer.

Tkatchenko, I., (1977) "Catalytic Reactions Involving Butadiene. I. Selective Dimerization to 4-Vinylcyclohexene with Polymetallic Precursors," *J. Organomet. Chem.*, 124:39-42.

Train, R. E., (1976) "Organic Chemicals Manufacturing Point Source Category" *Fed. Regist.* 41:1130-12.

Ulaneck, C. A., (1968) "Elastomers By Radical and Redox Mechanisms," in Kennedy, J. P. and Tornqvist, E., Polymer Chemistry of Synthetic Elastomers. Interscience Publishers, N.Y., pp. 127-183.

U.S. Int. Trade Comm., (1973-1977) "Synthetic Organic Chemicals U.S. Production and Sales" U.S. Int. Trade Comm. Publ. 833.

- U.S. Tarrif Comm. (1966-1972) "Synthetic Organic Chemicals" Traffic. Comm. Publ. 248.
- U.S. Bureau of the Census, (1965-1976a) "U.S. Imports for Consumption and General Imports," Report FT 246.
- U.S. Bureau of the Census, (1972-1976b) "U.S. Exports Schedule B commodity groupings," Vol. Ft.
- Van Duuren, B. L., (1965) "Carcinogenic Epoxides, Lactones and Hydroperoxides," in Wogan, G. N. (ed.) Mycotoxins in Foodstuffs, Cambridge, M.I.T. Press, pp. 275-285.
- Van Duuren, B. L., Nelson, N., Orris, L., Palmes, E. D. and Schmitt, F. L., (1963) "Carcinogenicity of Epoxides, Lactones, and Peroxy Compounds," J. Nat. Cancer Inst., 31:41-55.
- Van Duuren, B. L., Langsteth, L., Orris, L., Teebor, G., Nelson, N. and Kuschner, M., (1966) "Carcinogenicity of Epoxides, Lactones and Peroxy Compounds. IV. Tumor Response in Epithelial and Connective Tissue in Mice and Rats," J. Nat. Cancer Inst., 37:825-838.
- Van Duuren, B. L., Orris, L. and Nelson, N. (1965) "Carcinogenicity of Epoxides, Lactones and Peroxy Compounds Part II.," J. Nat. Cancer Inst., 35:707-717.
- Vinokurova, M. I., (1969) ("Combined Effect of Styrene, Butadiene, and Ethylbenzene on the Functional Indexes of the Cardiovascular System") Tr. Azerb. Nauch.-Issled. Inst. Gig. Tr. Proff. Zabol., 4:21-6 (Russian); Chem. Abstr. 81:140347r.
- Voklova, Z. A. and Bagdinov, A. M., (1969) ("Industrial Hygiene Problems in Vulcanization Processes of Rubber Production") Gig. Sanit., 34:33-40 (Russian).
- Volkova, A. A., Milkov, L. Y., Lupukhova, K. A., Malyar, L. M., Makarenko, Y. L., and Shakhova, T. K., (1970) ("Working Conditions and State of Health of Workers Employed in the Processes of Hot Vulcanization of Rubber for Footwear") Gig. Tr. Prof. Zabol. 14(1):31-34 (Russian).
- Von Oettingen, W. F., (1940) Toxicity and Potential Dangers of Aliphatic and Aromatic Hydrocarbons, Public Health Bulletin No. 255., U.S. Public Health Service, 25-28.
- Warning, R. H., (1971) "The Metabolism of Cyclo-octadiene, 1,3-Cyclo-octadiene and 1,5-Cyclo-octadiene in the Rat and Rabbit, and the Reaction of these Compounds with Glutathione in vivo in the Rat," Xenobiotica 1(3):303-308.
- Watkinson, R. J. and Somerville, H. J., (1975) "The Microbial Utilization of Butadiene," Proc. Int. Biodegrad. Symp. 3:35-42.
- Weast, R. C. (ed.) (1973) Handbook of Chemistry and Physics, CRC Press, Cleveland, Ohio.

Webber, L. A. and Burks, C. E. (1952) "Determination of Light Hydrocarbons in Water," Anal. Chem., 24(7):1086-1087.

Weyker, R. G., (1960) "Process for Anthraquinones from Naphthalene via Naphthoquinone," U.S. Patent 2,938,913.

Wilke, G. (1963) "Cyclooligomerization of Butadiene and Transition Metal π -Complexes," Angw. Chem., 2(3):105-164.

Wilson, R. H., (1944) "Health Hazards Encountered in the Manufacture of Synthetic Rubber," J. Am. Med. Assoc., 124(11):701-703.

Woerner, R. C., (1967) "Combined Method of Disposal of Waste and Purification of Chemical Product," U.S. Patent 3,336,414.

CONCLUSIONS AND RECOMMENDATIONS

A. Butadiene

The available literature indicates that butadiene is a compound of low toxicity and minimal environmental impact. Additional data would be desirable to supplement this conclusion, particularly for the following specific areas:

i) metabolism - metabolites of butadiene have not been positively identified. This is potentially important, because two suspected metabolites have shown carcinogenic activity.

ii) chronic toxicity - long-term studies would be desirable to resolve the discrepancy between U.S./Western European reports of few adverse effects at high concentrations and Eastern European studies showing some toxic effects at low levels. Further research, however, should not duplicate the on-going chronic-exposure study at Hazleton Laboratories Europe, sponsored by the International Institute of Synthetic Rubber Producers.

iii) mutagenicity - additional studies might be considered in other test systems besides bacteria.

iv) environmental monitoring - only a few studies measured the amount of butadiene released during phases of production and use. Additional studies would be desirable to determine if a potential problem exists, especially from fugitive losses.

v) environmental chemistry - the reactions of butadiene under conditions other than urban air might be investigated.

B. Butadiene oligomers

Fewer data are available for butadiene oligomers. Vinylcyclohexene, because it is present as an impurity in butadiene, appears to be the more important oligomer for further study. Possible carcinogenic effects have been

noted in a skin application study (although they may have been due to an impurity present in the vinylcyclohexene). Another carcinogenesis study is indicated; the National Cancer Institute is planning to begin an assay in October, 1978. However, additional information would be desirable for all oligomers in the following broad categories where almost no data exist:

- i) biological effects
- ii) environmental exposure - it currently is not possible to assess the environmental effects of the oligomers as no data are available.

Appendix A

Summary of Sources Employed

References used in this report were selected from searches of automated information retrieval systems, indices, standard references works, journals, books, etc. Manufacturers, researchers, and federal and state agencies, among others, were contacted directly.

The following is a list of on-line systems searched:

- Biological Abstract
- Cancerline
- Chemical Abstracts Condensates
- Chemical Industry Notes
- Economic Information System
- Enviroline
- Federal Index
- Federal Index Weekly
- Food and Science and Technology Abstracts
- Marketing Abstracts
- Marketing Abstracts Weekly
- National Technical Information System
- Ocean Abstracts
- Pollution Abstracts
- Smithsonian Science Information Exchange
- Science Citation Index
- Toxline
- Toxback
- Water Resources Abstracts

Also, the Technical Information Center data base was searched by the National Institute of Occupational Safety and Health.

Manually searched indices included:

- Biological Abstracts (1959-1970)
- Chemical Abstracts (1957-1971)
- Excerpta Media
 - Cancer (1953-1977)
 - Pharmacology and Toxicology (1965-1977)
 - Development Biology and Teratology (1965-1976)
 - Environmental Health and Pollution Control (1972-1976)
 - Occupational Health and Industrial Medicine (1971-1976)
- Index Medicus (1957-1977).

Appropriate books and compendia were examined. In addition, current journals were screened. The literature search is considered complete through June, 1978.

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